Columbia University in the City of New York

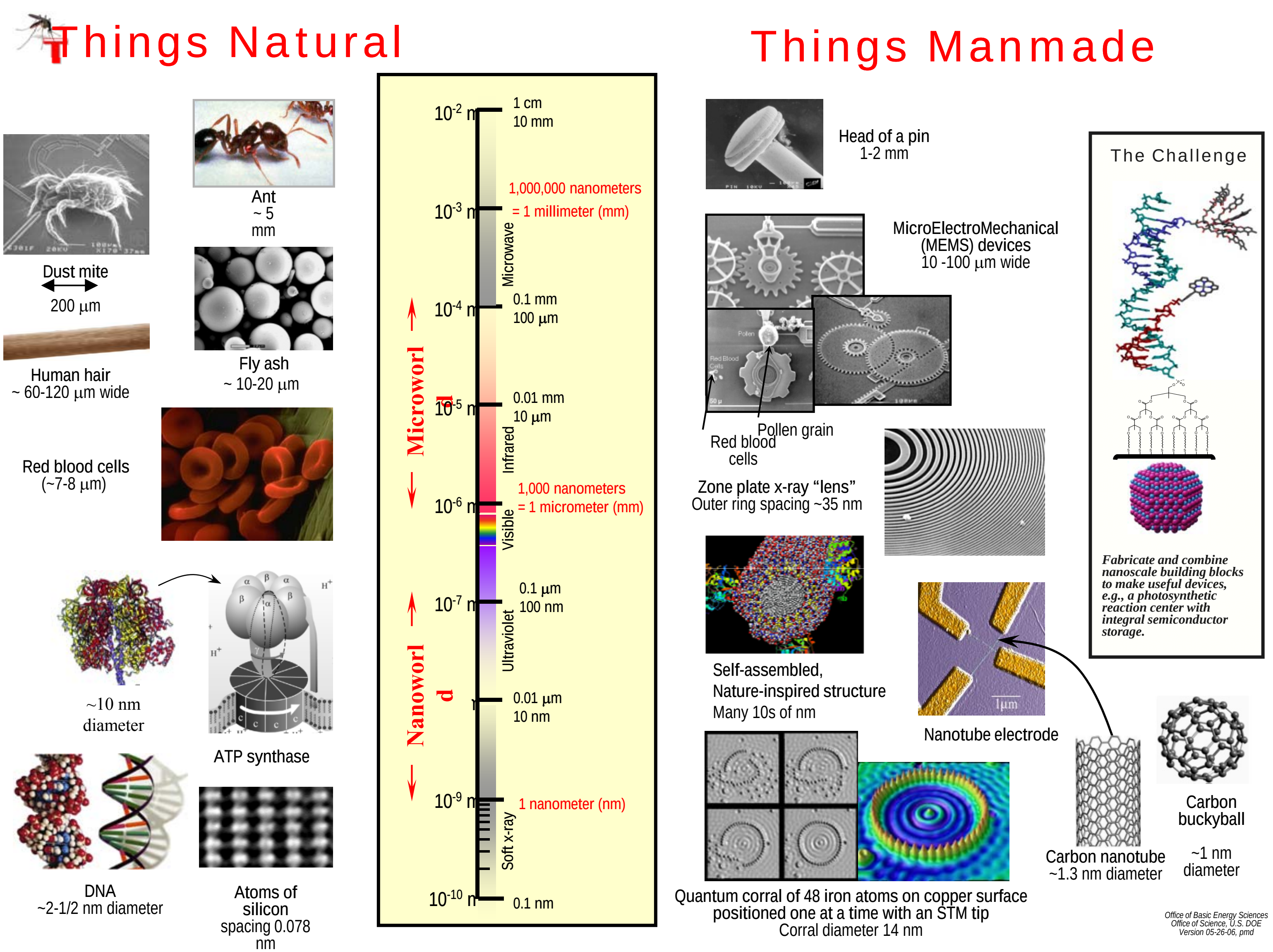
2012 Einstein Scholar Lecture for Chinese Academy of Sciences

Peking University, May 21
CAS National Center for Nanoscience and Technology, Beijing, May 17
CAS Suzhou Institute for Nanotechnology & Nano-bionics, May 11

New Columbia Interdisciplinary Science Building 2011

- This tutorial lecture describes unifying and basic principles of nanoscience, and also presents our most recent research on graphene highly doped by interfacial charge transfer.

The Scale of Things – Nanometers and More



Things Natural

Dust mite
200 µm

Ant
~ 5
mm

Human hair
~ 60-120 µm wide

Fly ash
~ 10-20 µm

Red blood cells
(~7-8 µm)

~10 nm
diameter

ATP synthase

DNA
~2-1/2 nm diameter

Atoms of
silicon
spacing 0.078
nm

Things Manmade

Head of a pin
1-2 mm

MicroElectroMechanical
(MEMS) devices
10 -100 µm wide

Red blood
cells

Pollen grain

Zone plate x-ray "lens"
Outer ring spacing ~35 nm

Self-assembled,
Nature-inspired structure
Many 10s of nm

Nanotube electrode

Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm

Carbon nanotube
~1.3 nm diameter

Carbon
buckyball

~1 nm
diameter

The Challenge

Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

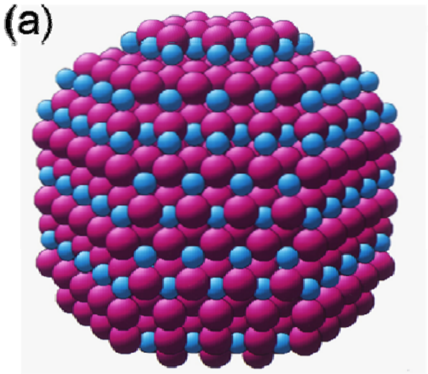
Office of Basic Energy Sciences
Office of Science, U.S. DOE
Version 05-26-06, pmd

carbon nanotubes

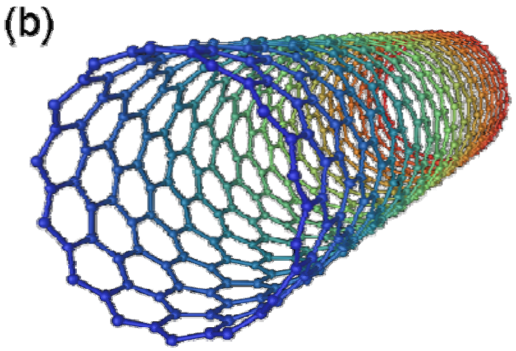
semiconductor nanocrystals

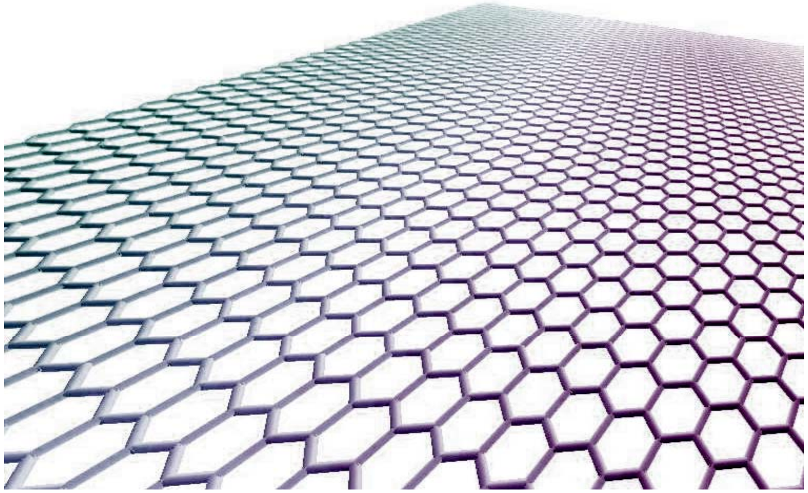
Nanoscience: Graphene, Carbon Nanotubes and Semiconductor Nanocrystals

Louis Brus
Columbia University
New York, NY



CdSe
Nanocrystal



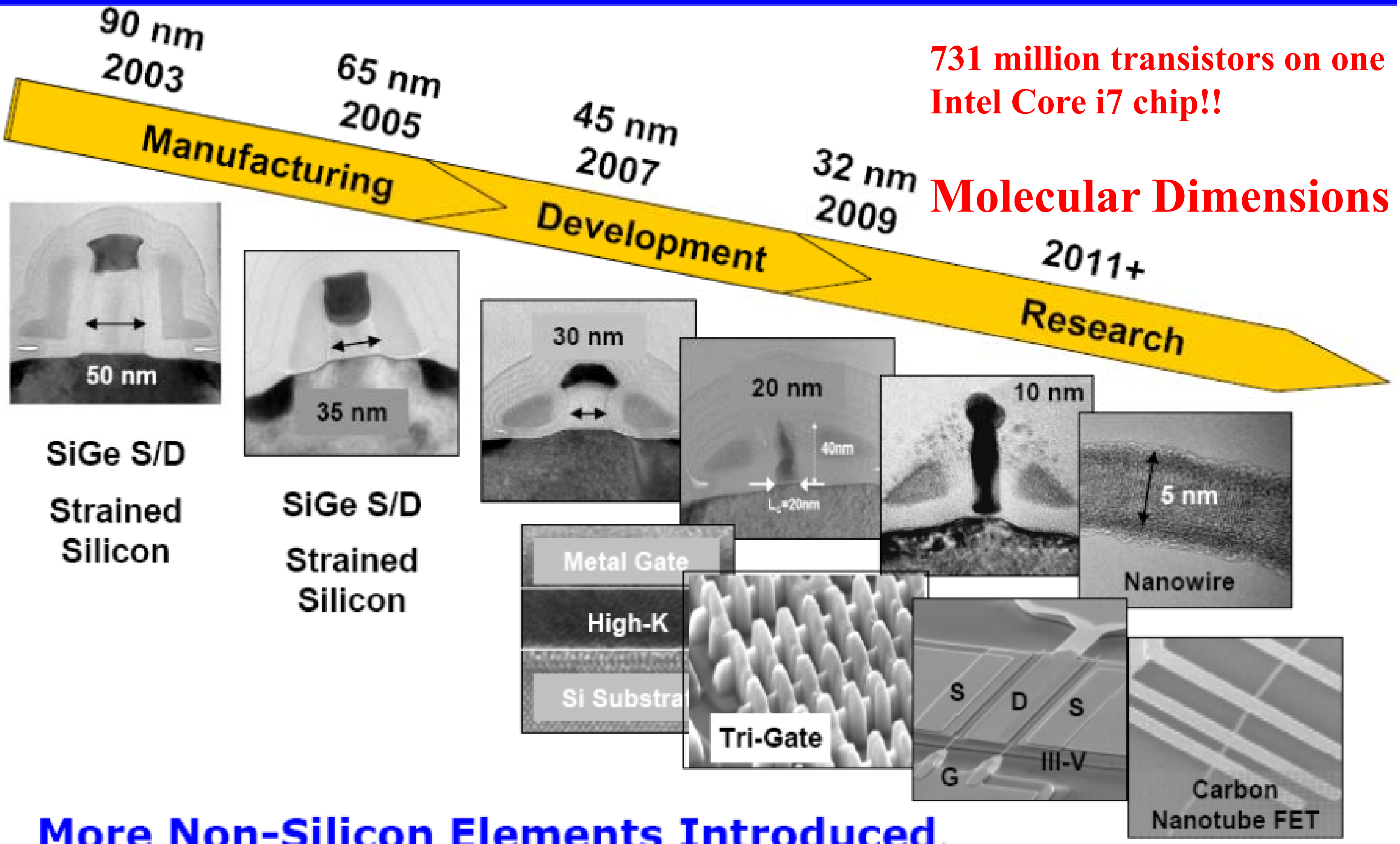


Graphene Electron Correlation and Charge Transfer

1. Single electron electronic structure, optical Properties and Electron Correlation in Graphene: comparison with Nanocrystals and SWNT.

2. Charge Transfer Doping and Fermi Level Shift by Adsorbed and Intercalated Species. Asymmetric doping on one side only. Extreme Electron Doping by Alkali atoms.

Transistor Nanotechnology



90 nm
2003

65 nm
2005

45 nm
2007

32 nm
2009

2011+

Manufacturing → **Development** → **Research**

SiGe S/D

Strained
Silicon

SiGe S/D

Strained
Silicon

731 million transistors on one Intel Core i7 chip!!

Molecular Dimensions

More Non-Silicon Elements Introduced →

Intel Corp.

Future options subject to change

Nanoscience: The evolution from molecules to bulk crystals

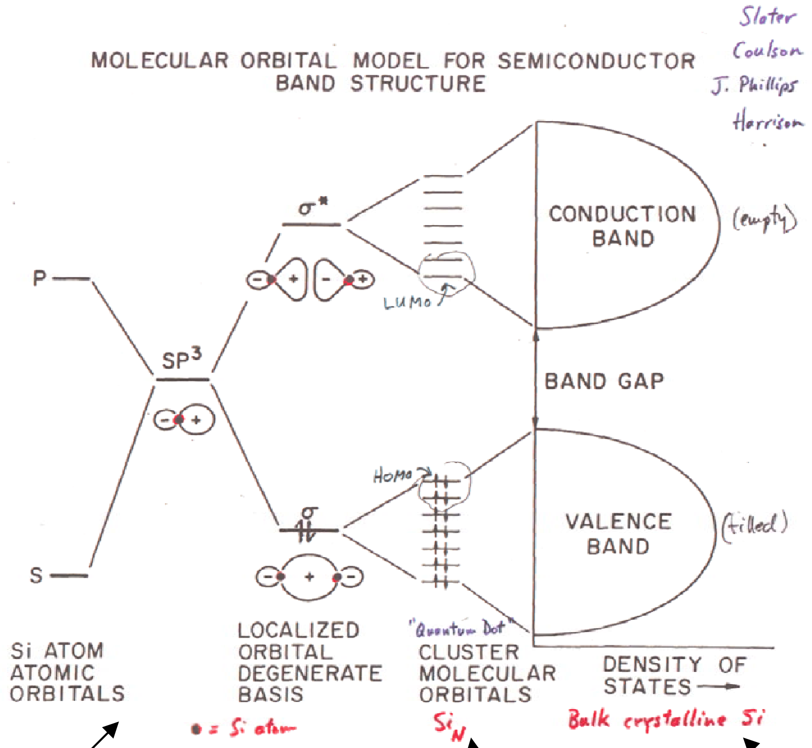
Intellectual challenge: how to quantitatively describe electronic properties as a function of size? Physics concepts? Chemistry concepts?

Synthetic challenge: can we actually make well defined nanocrystals and nanotubes ? Can we vary the surface chemistry?

Characterization challenge: can we measure physical properties one nanocrystal or nanotube at a time?

Technology Challenge: Nanocrystals and Nanotubes are new families of large molecules. Can we use them in technology?

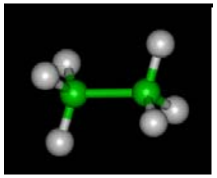
Electrons: Evolution from Molecular Orbitals to Continuous Bands



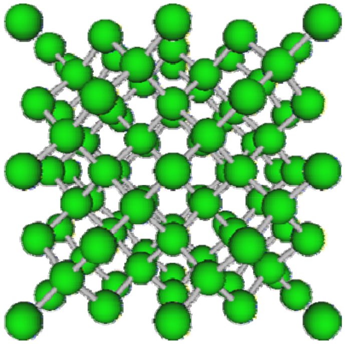
Local chemical bonding around each Si atom is the same in the molecule and crystal – tetrahedral covalent sp3 hybridization

Nanometer crystallite should have larger band gap than bulk crystal

Bulk Crystalline Silicon

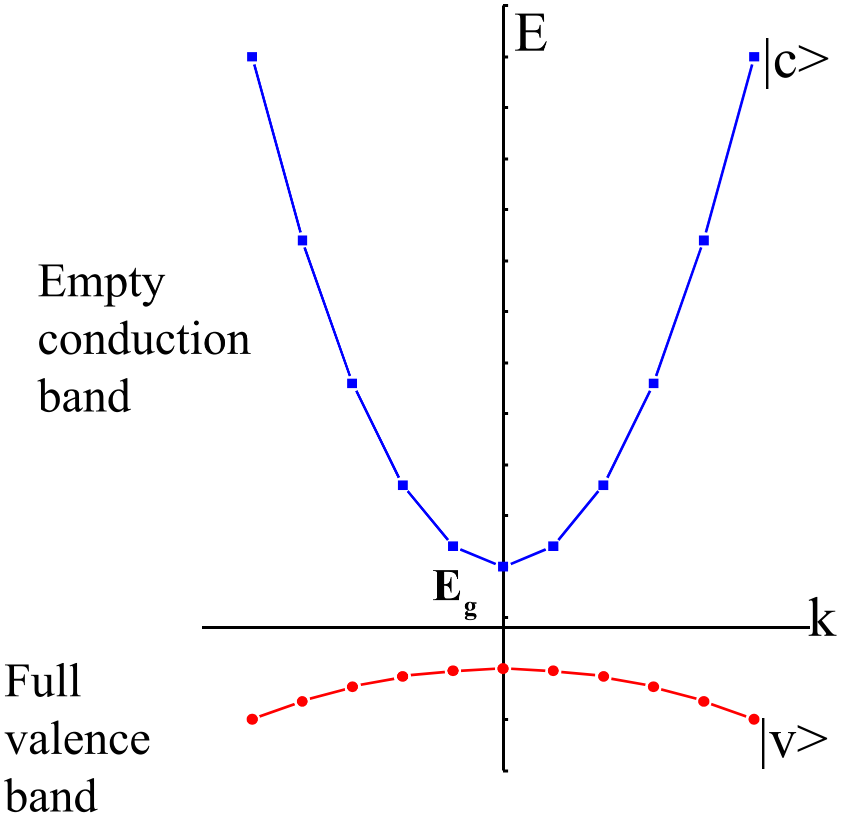


Disilane molecule



Silicon Nanocrystal

Quantum Size Effect – "Particle in a box"



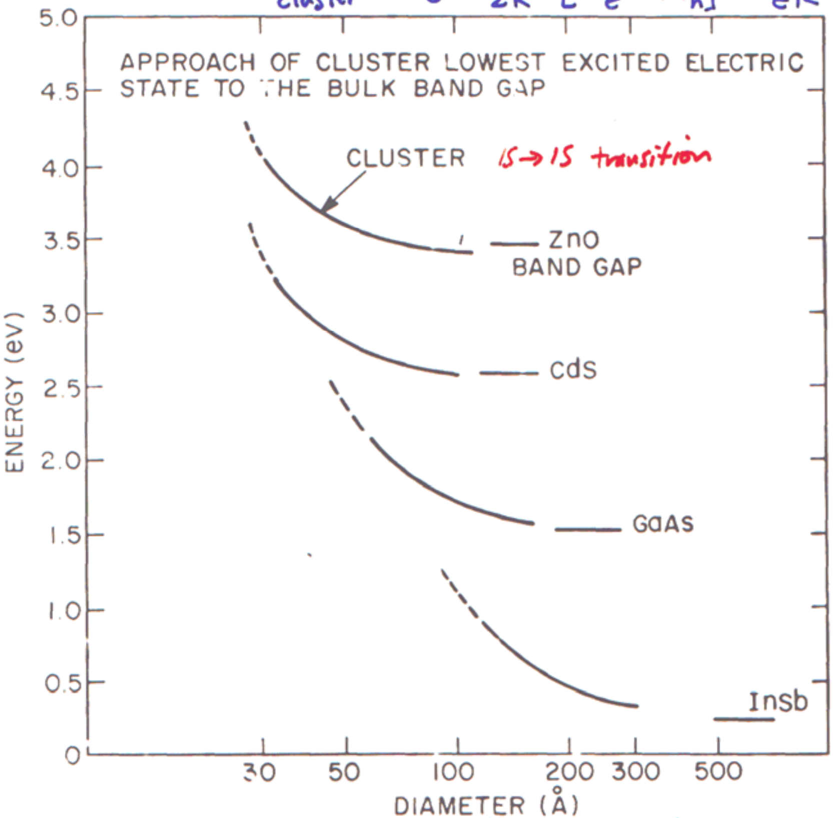
De Broglie Electron Momentum
mv=hk=h/λ

electron wavelength λ quantized in particle

Electron Correlation – Coulomb attraction between e^- and h^+

$$\Psi \simeq \phi_{1s}(r_e)\,\phi_{1s}(r_h) \quad \text{zero order}$$

$$E^*_{cluster} = E_g + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\epsilon R} +$$



No adjustable parameters!

L. Brus, J. Chem. Phys. 79, 5566 (1983); 80, 4403 (1984)

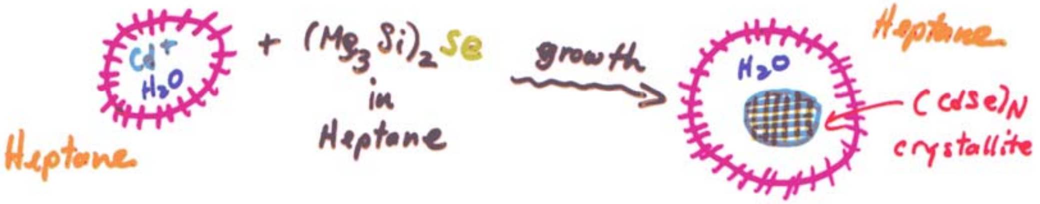
Synthesis 1986 Steigerwald etal, JACS 110, 3046 (1988)

Organometallic synthesis, controlled Growth, Surface "capping"

and isolation of stabilized clusters

A] Take advantage of hydrocarbon phase – hydrophobic reagents

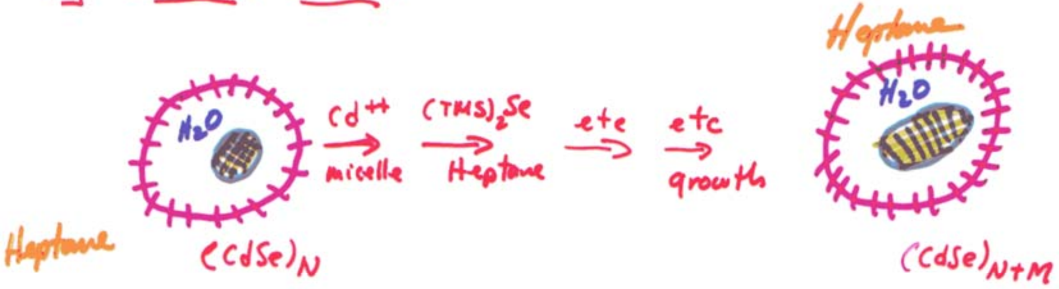
* Mike Steigerwald
Paul Alivisatos
Lou Brus



small 18 Å $N \simeq 70$
large 50 Å $N \simeq 630$
standard deviation 20%

dry → redissolve → heptane colloid

B] Controlled Growth



Crystallite in micelle, with water present, is stable yet can grow further

⟹ exotic chemistry on surface

⟹ concentric growth of one material on another

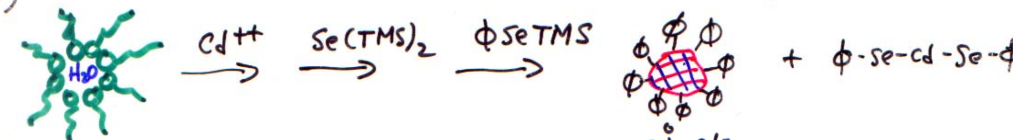
Synthesis 1988 Bawendi etal J. Chem. Phys. 91, 7282 (1989)

Two Step Organometallic Synthesis of CdSe Single Crystallites

(Mike Steigerwald)

(Moungi Bawendi)

1)



heptane

inverse micelle

10-15 Å CdSe

pale yellow powder

2)

pale yellow powder

$\xrightarrow[\text{90\% } Bu_3P \text{, 10\% } Bu_3PO \text{, Ar}]{\text{Reflux 230°C, 3 hours}}$

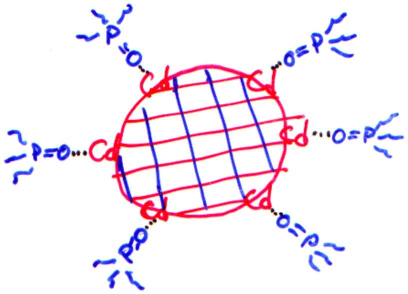
Reflux 230°C

3 hours

90% Bu_3P

10% Bu_3PO

Ar



"capped

32 Å

clear red solution

fluorescence

Characterization

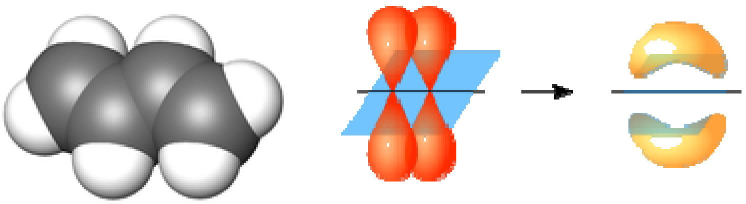
TEM	Pat Carroll
Powder X-ray	Refik Kortan
^{77}Se NMR	Peter Reynders
Se, Cd EXAFS	Matt Marcus

Carbon Nanoscience

Graphene and Single Wall Carbon Nanotubes

Hückel molecular orbitals for P electrons

Butadiene

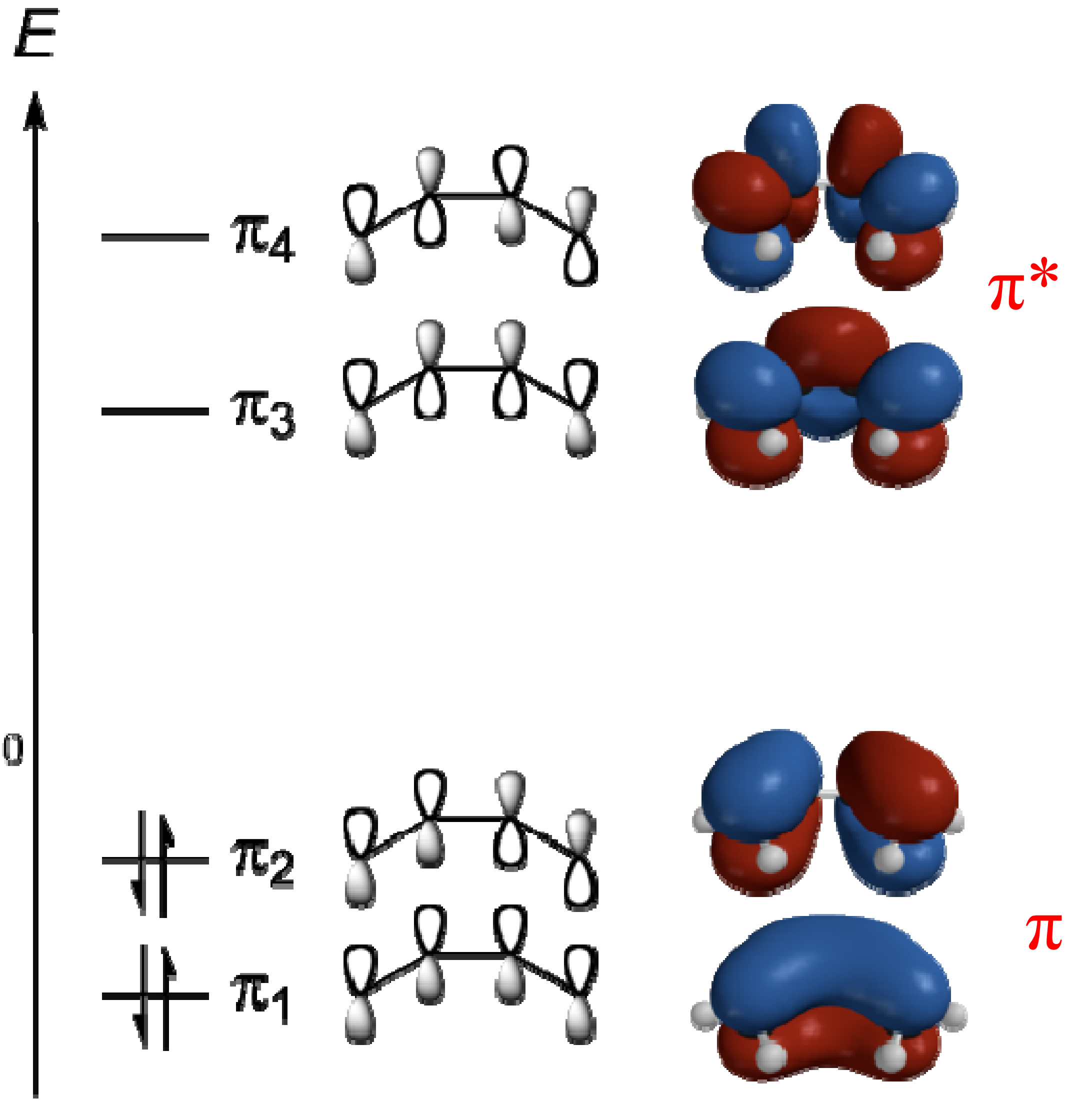


$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

$$(\alpha - E)(\alpha + \beta - E) - \beta^2 = 0$$

$$E\pm = \alpha + \frac{1 \pm \sqrt{5}}{2}\beta$$

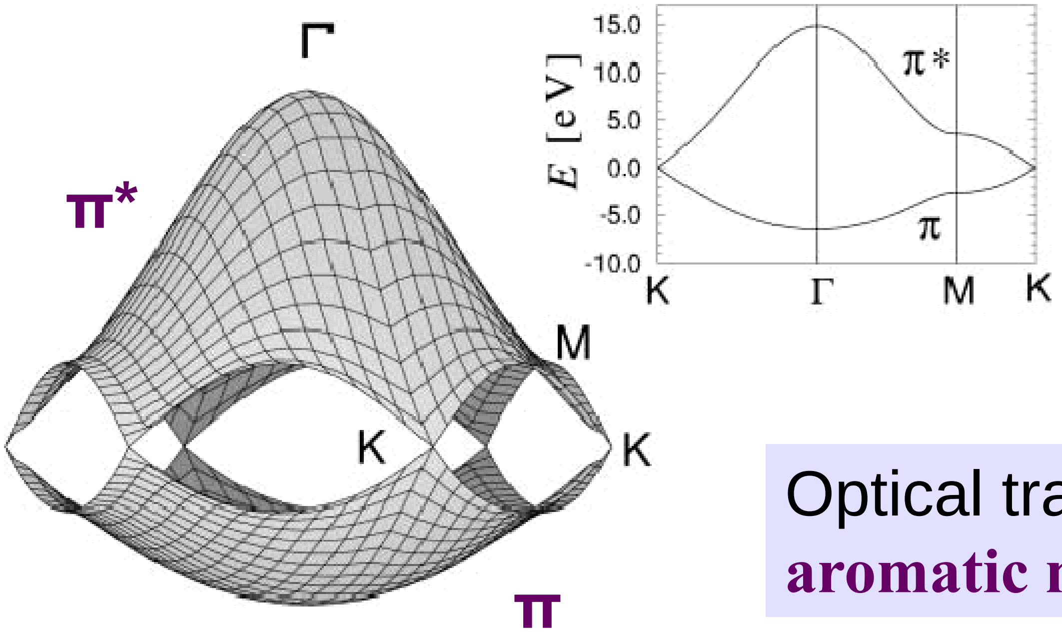


From Wikipedia

Huckel π and π* MOs (Band structure) of graphene

Molecular Orbital Energies are a function of electron momentum k(x,y) in the plane of graphene

Electron momentum k is continuous for infinite plane of graphene

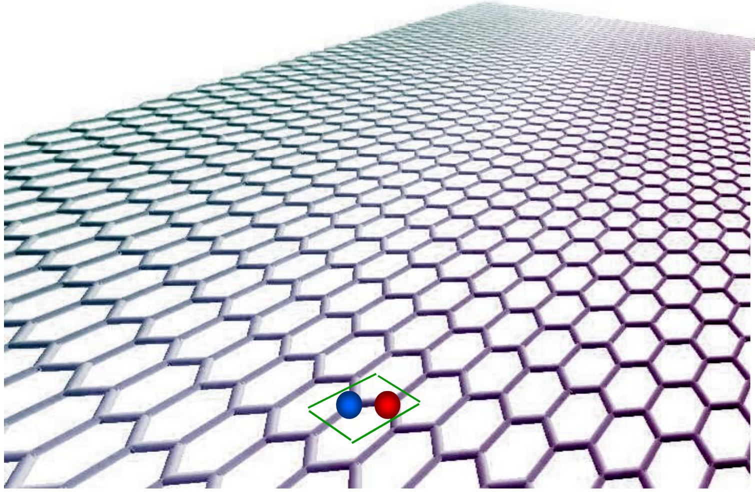


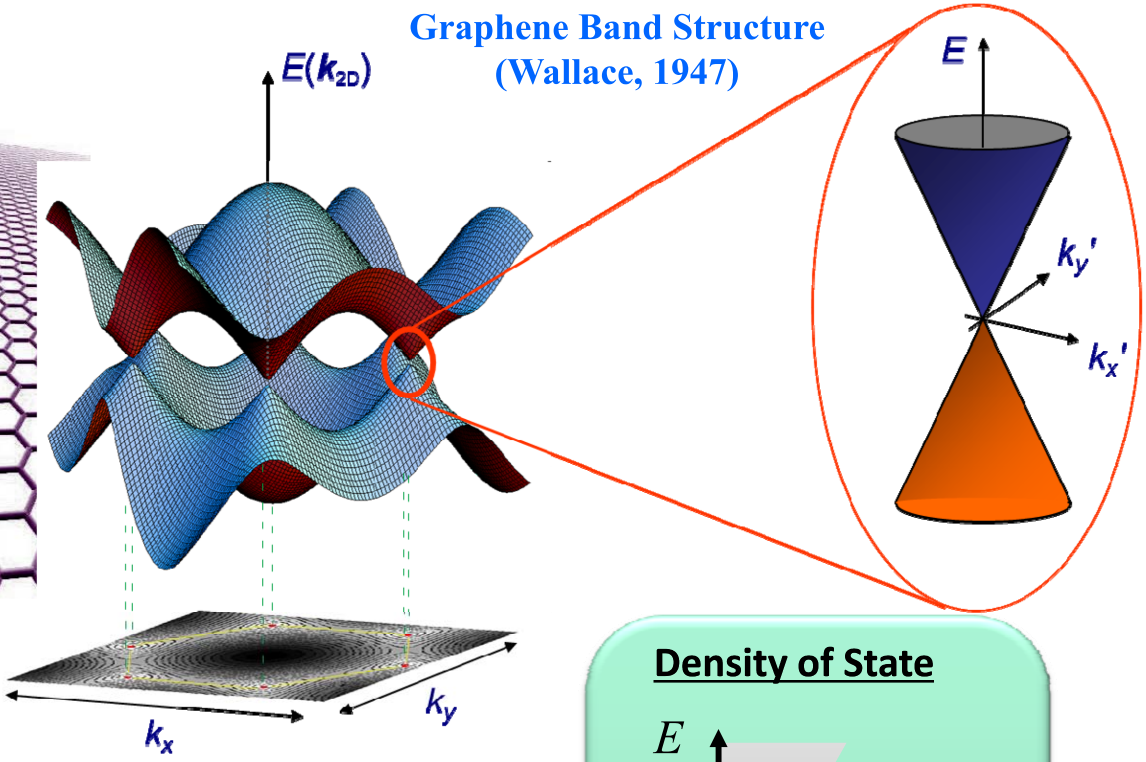
beta = 3.033 eV
Resonance integral

Optical transitions: **π to π* just as in aromatic molecules**

Saito and Kataura, *Topics Appl. Phys.* **2001**, *80*, 213

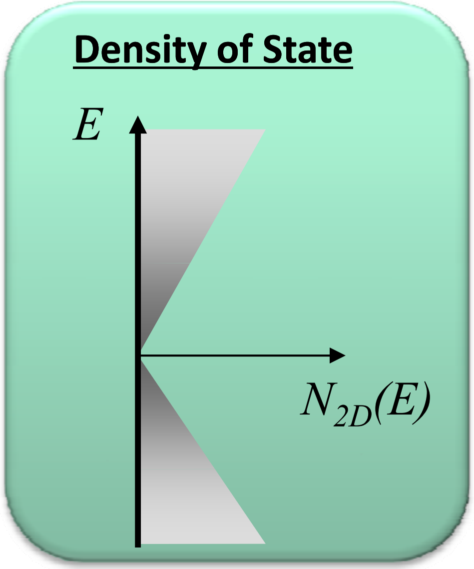
Graphene: atomically thin SP_2 carbon network





Graphene Band Structure (Wallace, 1947)

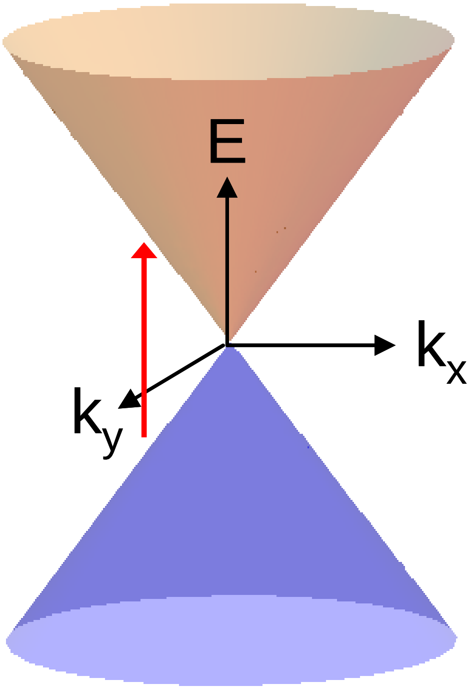
- Atomically thin 2D system
- Zero carrier mass: high mobility
- Graphene is zero-gap semiconductor
- Density of State is zero at $E = 0$.



Density of State

Philip Kim

Graphene electronic absorption
π interband transitions



No band gap – continuous absorption in IR, visible, and UV

Optical (sheet) conductivity:

$$\sigma^{(1)}(\omega) = \frac{\pi e^2}{2h} = (\pi/4)\, G_0$$

Optical absorption:

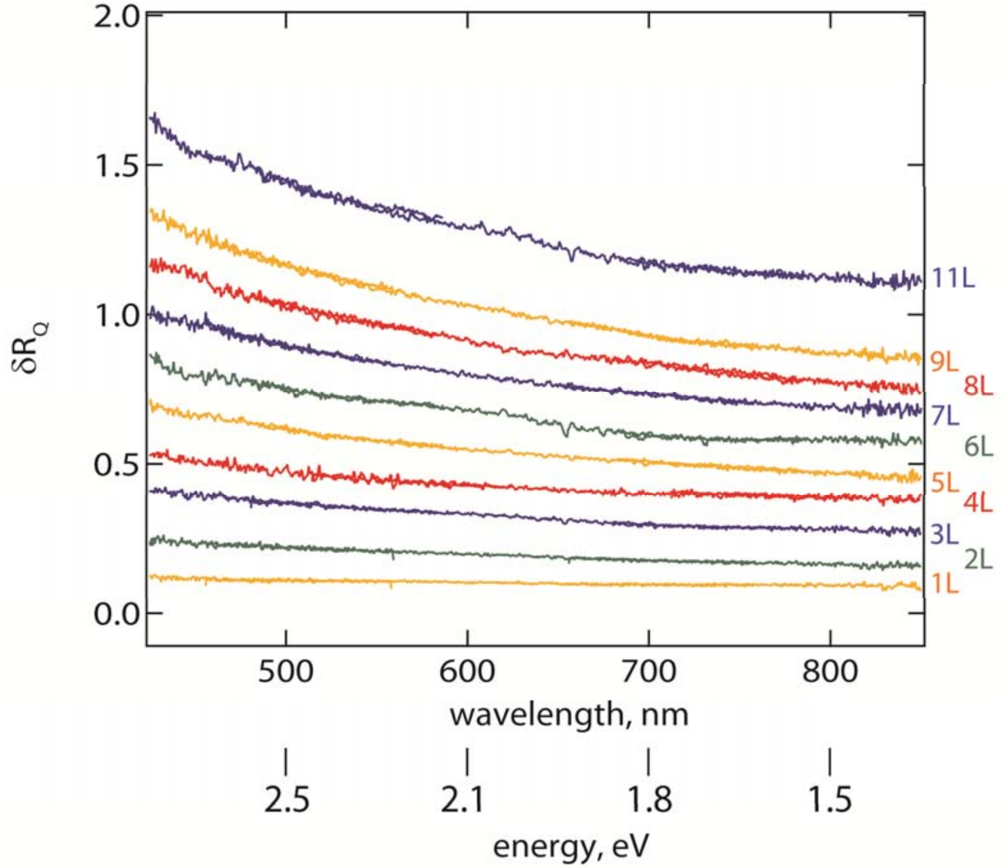
$$A(\omega) = \frac{\pi e^2}{\hbar c} = \pi\alpha = \frac{\pi}{137} = 2.3\%$$

Mak and Heinz

V. P. Gusynin et al., PRL 96, 256802 (2006)
S. Ryu et al., PRB 75, 205344 (2007)
D. S. L. Abergel et al., PRB 75, 155430 (2007)

Continuous electronic absorption across the IR, Visible and Ultraviolet
No band gap

Graphene on Quartz

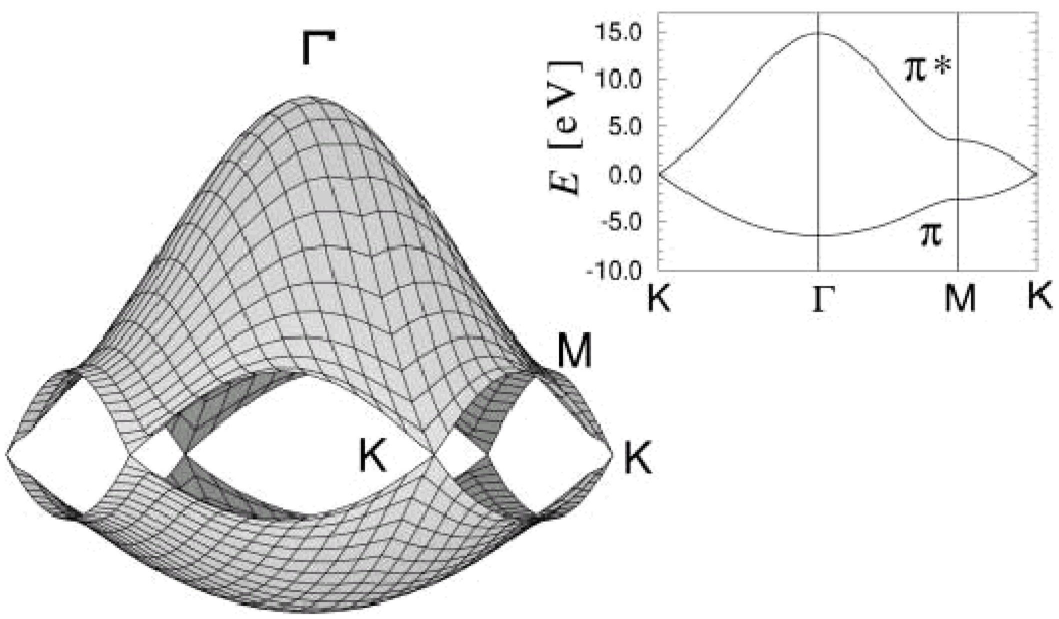


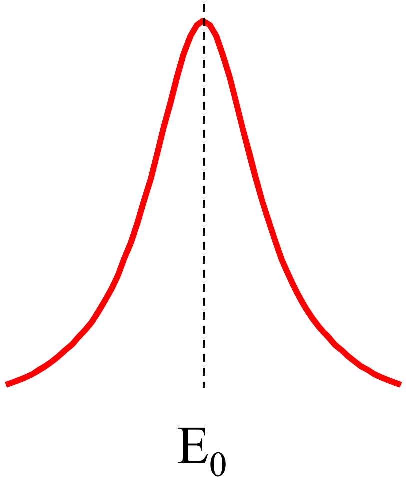
$$\delta R_Q = \frac{4}{n^2_{sub} - 1} A$$

2.6 % per layer
at 800 nm

Absorption increases in UV at M saddle point

Independent electron model: no correlation



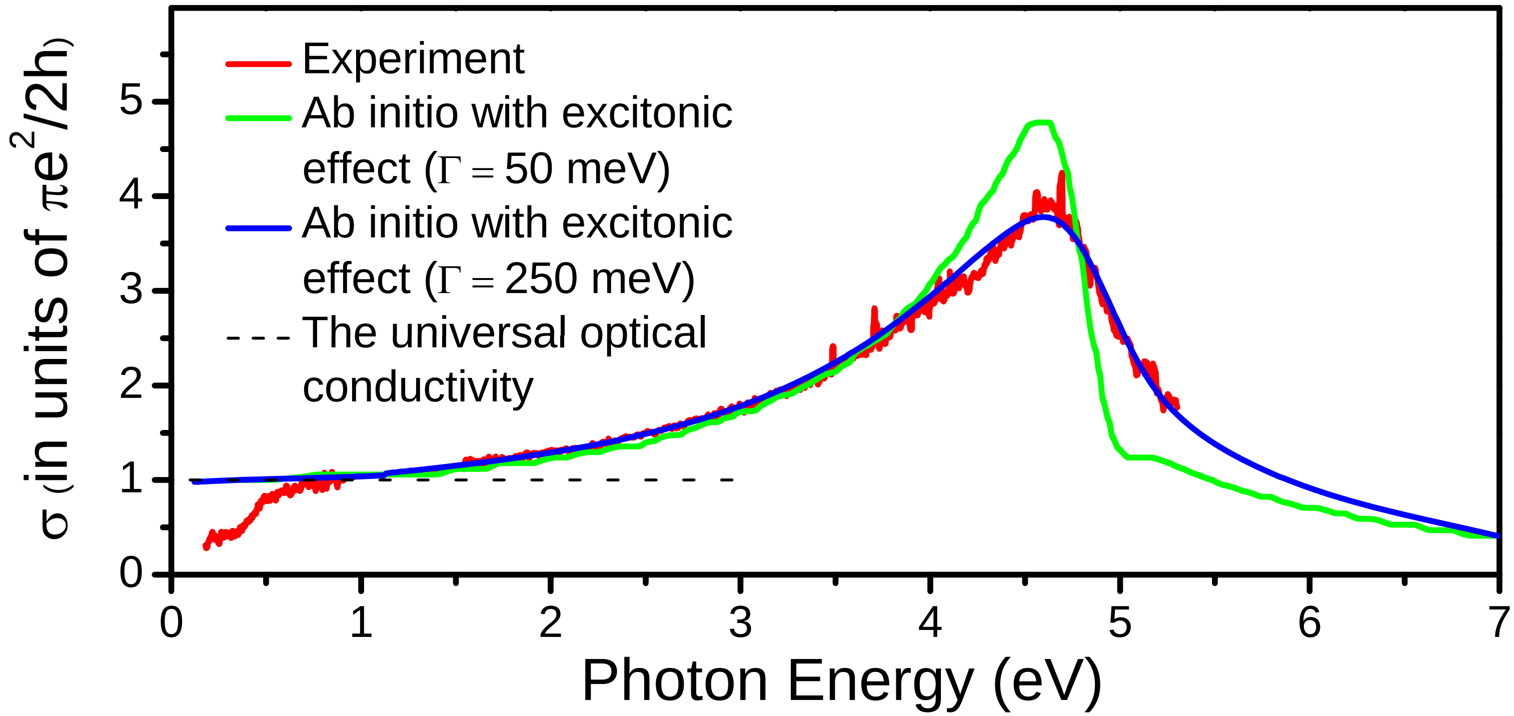


$$DOS^{2D}_{SP}(\omega) \propto -\ln\left|1-\frac{\omega}{E_0}\right|$$

Symmetric line shape
near the saddle point, **assuming**
no electron correlation

Mak and Heinz

An Exciton (electron-hole bound state) with 0.25eV Binding Energy forms at the M saddle point, even though the system is metallic



Existence of strong e-h interactions at the graphene saddle point

Quasiparticles' lifetime near the M-point ~ 2.6 fs

Also Chae etal, (von Klintzing group) Nano Lett. (2011) 11, 1379.

Fano lineshape at saddle point

Mak and Heinz

Yang et al. PRL 103, 186802 (2009)

Strong Correlation: Graphene Fractional quantum Hall effect at low temperature

Andre Geim & Philip Kim

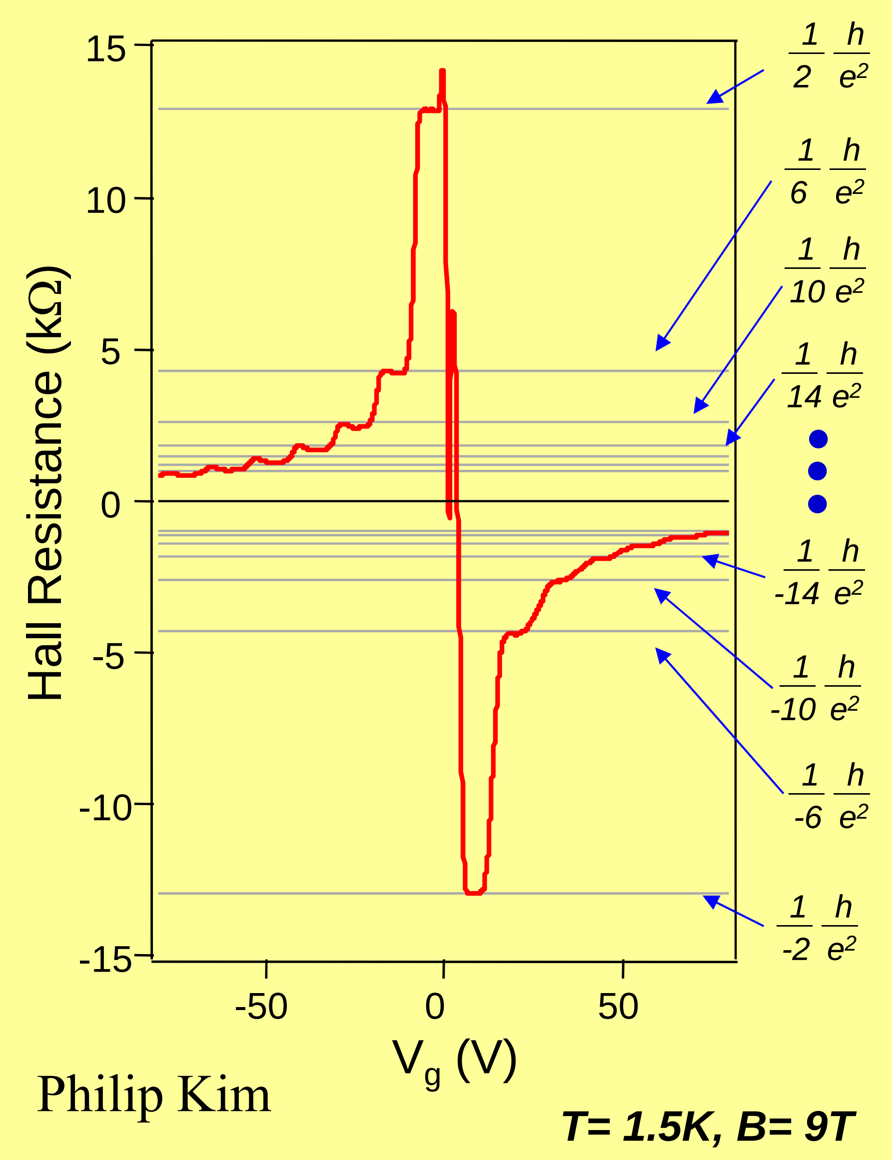
Classic signature of Correlated Electron Motion at low temperature

Robust effect implies that electron-electron interactions are essentially unscreened.

Bolton et al, Nature 2009, 462, 192
Du et al, Nature 2009, 462, 192.

Remarkable properties all result from strong aromatic pi chemical bonding

Fractional Quantum Hall Effect



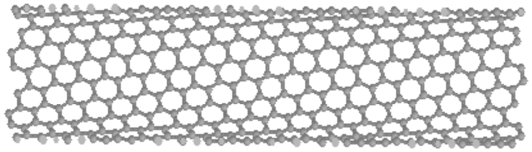
Philip Kim

T= 1.5K, B= 9T

If electron correlation is strong in graphene, it should be stronger in semiconducting SWNT:

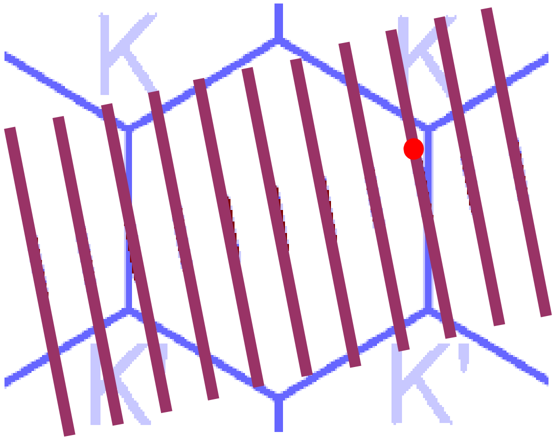
Lower dimensionality

Existence of a Band Gap; less screening



(7,12) Chiral Semiconducting Tube

Semiconductor Carbon Nanotubes
Independent Electron Model: no correlation

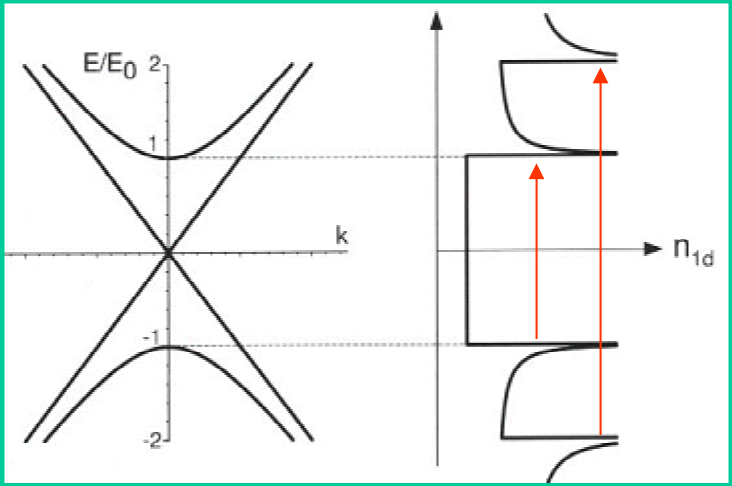


Size Quantization in Nanotubes:

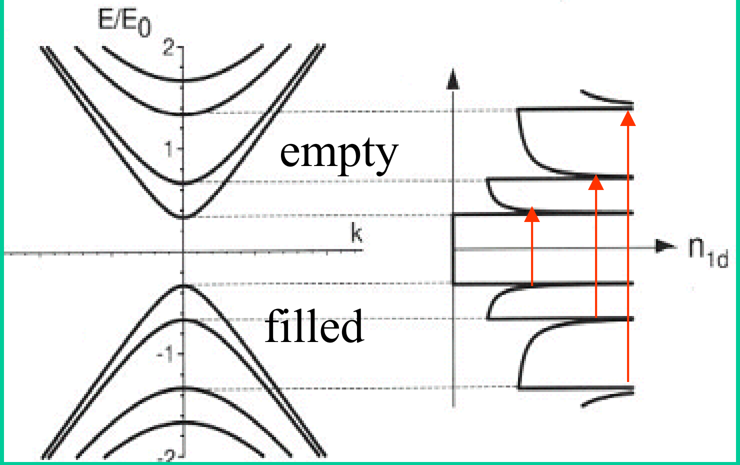
Electron momentum k quantized around circumference.

Electron momentum remains continuous along length

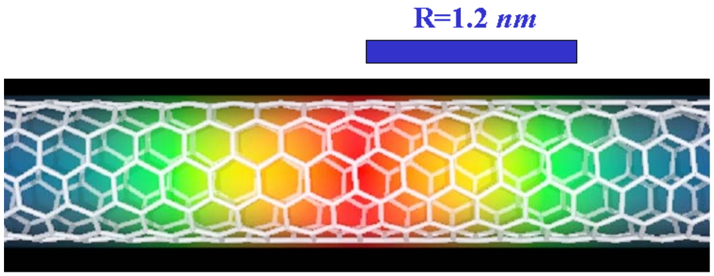
Metallic:



Semiconducting:

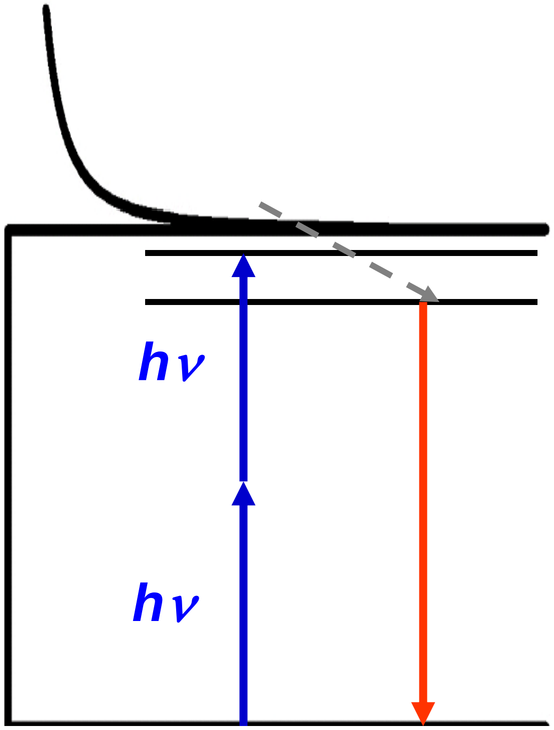


Correlation: Neutral Bound Excitons Due to electron-hole attraction



Exciton envelope wavefunction:

Neutral excited state moves as a unit along the SWNT



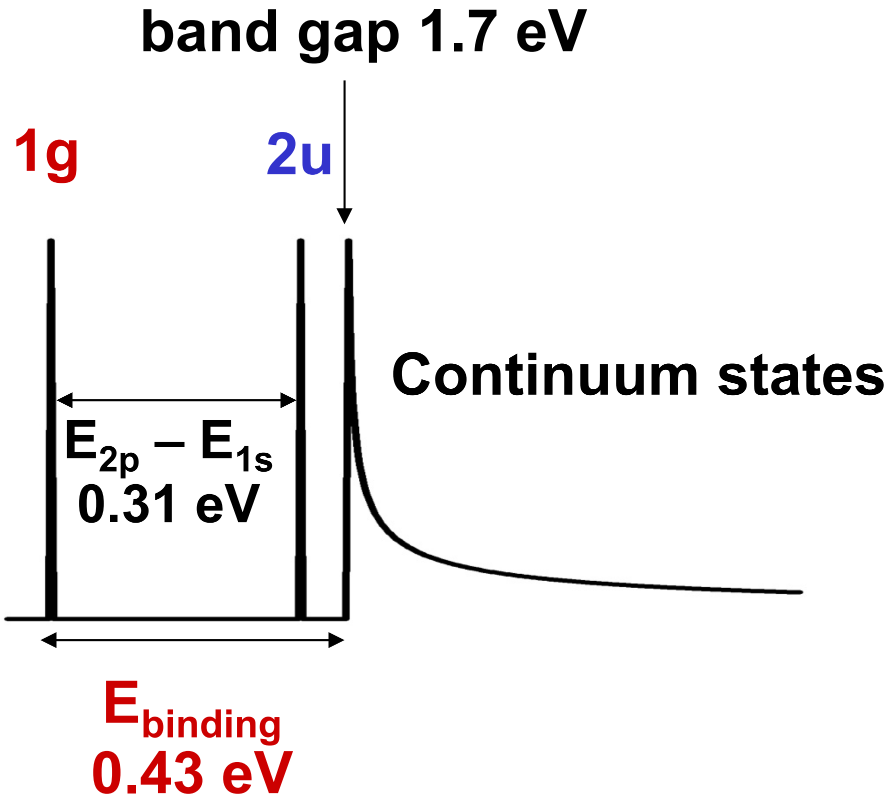
Exciton Bound states below the van Hove Band Edge

Two photon luminescence excitation spectra shows strongly bound exciton

F. Wang *etal*, Science 308, 838(2005)

(6,5) nanotube

d_t = 0.76 nm



band gap 1.7 eV

1g

2u

Continuum states

$E_{2p} - E_{1s}$
0.31 eV

$E_{binding}$
0.43 eV

For comparison:

Poly(phenylene vinylene) ~ 0.35 eV
Semiconductor nanowires ~ tens of meV

Why? Increased electron-electron interaction in Nanostructures

Two independent factors: dimensionality and screening

1. Dimensionality with no change in screening:

3D bulk semiconductor: weak Coulomb, excitons not important
2D confinement in plane: Coulomb interaction up by 4x
1D confinement on line: Coulomb interaction diverges!
Low Dimensionality implies increased electron-electron correlation

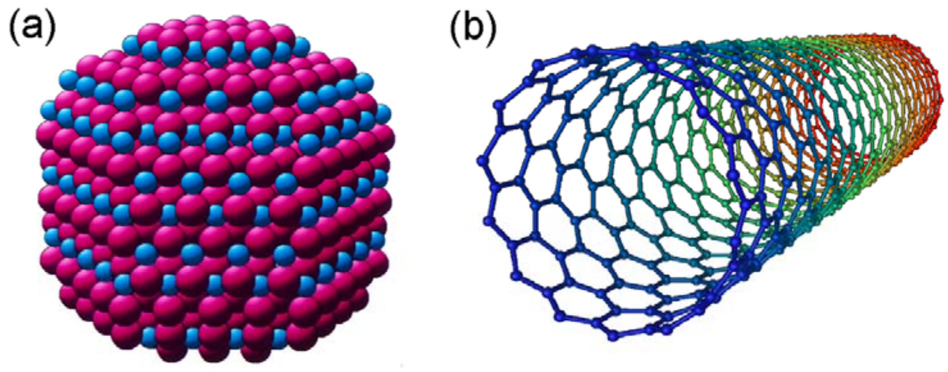
0D quantum dot is a different case: no dissociation, less correlated motion,
Finite Coulomb interaction, kinetic energies larger

2. Screening of Coulomb interaction:

reduced screening in 1D,
almost full screening in 0D
Reduced screening implies increased electron-electron correlation

Brus, Nano Letters 10, 363 (2010)

Quantum Dots compared to Carbon Nanotubes

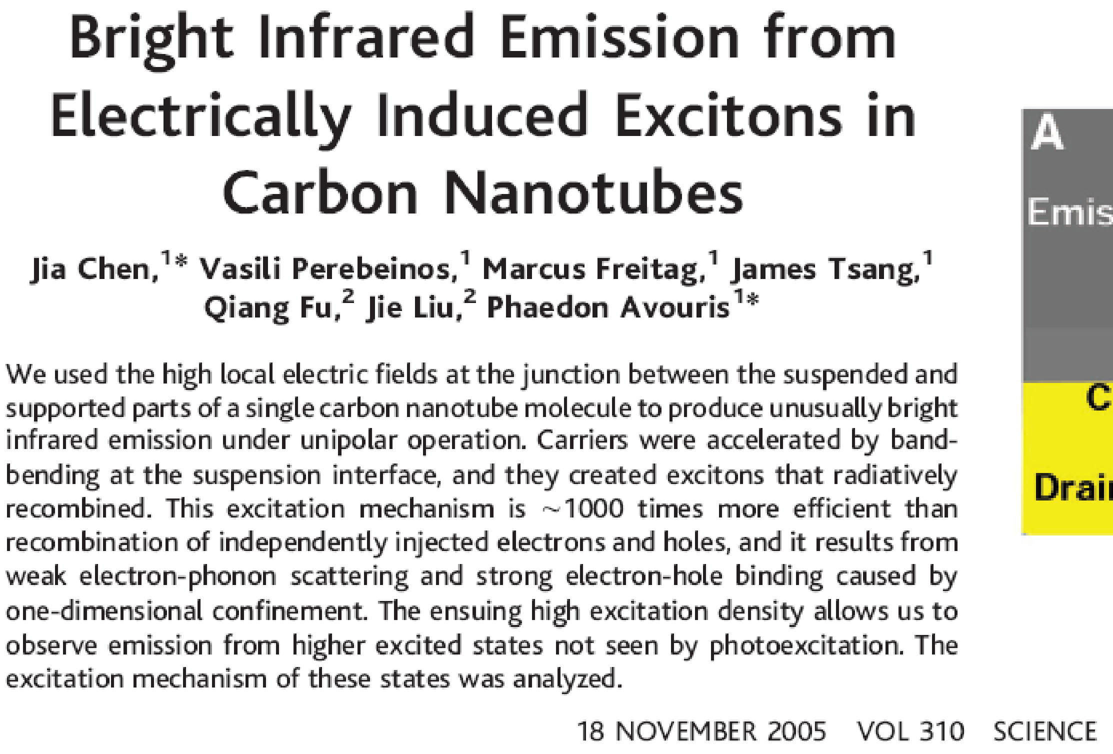


4nm CdSe nanocrytal	*1nm Carbon Nanotube*
Particle in box orbitals	*Plane wave basis orbitals*
Surface states and ligands	*No surface states or ligands*
Rigid structure	*Rigid structure: minor Franck-condon shift*
Hard to collect photocurrent	*Easy to collect photocurrent*
Band gap: 2. 2 eV	*Band Gap: 1.7 eV*
Kinetic energies 0.4 eV	*Kinetic Energies 0.4 ev*
Coulomb energy 0.1 eV	*Coulomb Energy: 0.8 eV*

Carbon Nanotubes apparently have the strongest electron-electron interaction of any Nanosystem

Enhanced impact ionization

Decay of accelerated “hot” electrons by exciton creation rather than phonon creation

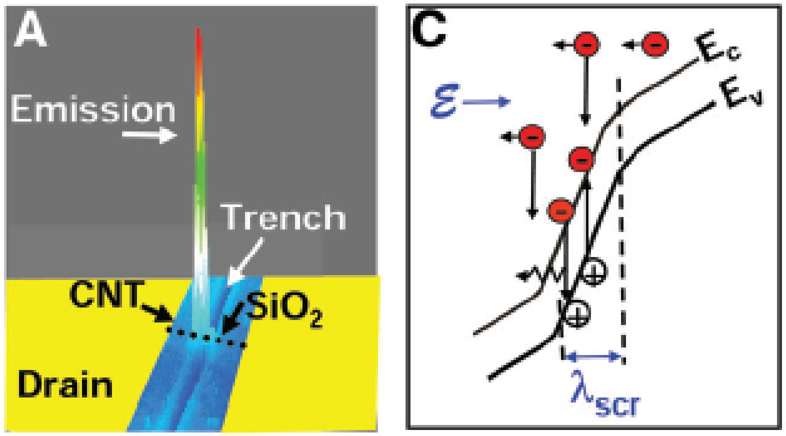


Bright Infrared Emission from Electrically Induced Excitons in Carbon Nanotubes

Jia Chen,[1*] Vasili Perebeinos,[1] Marcus Freitag,[1] James Tsang,[1]
Qiang Fu,[2] Jie Liu,[2] Phaedon Avouris[1*]

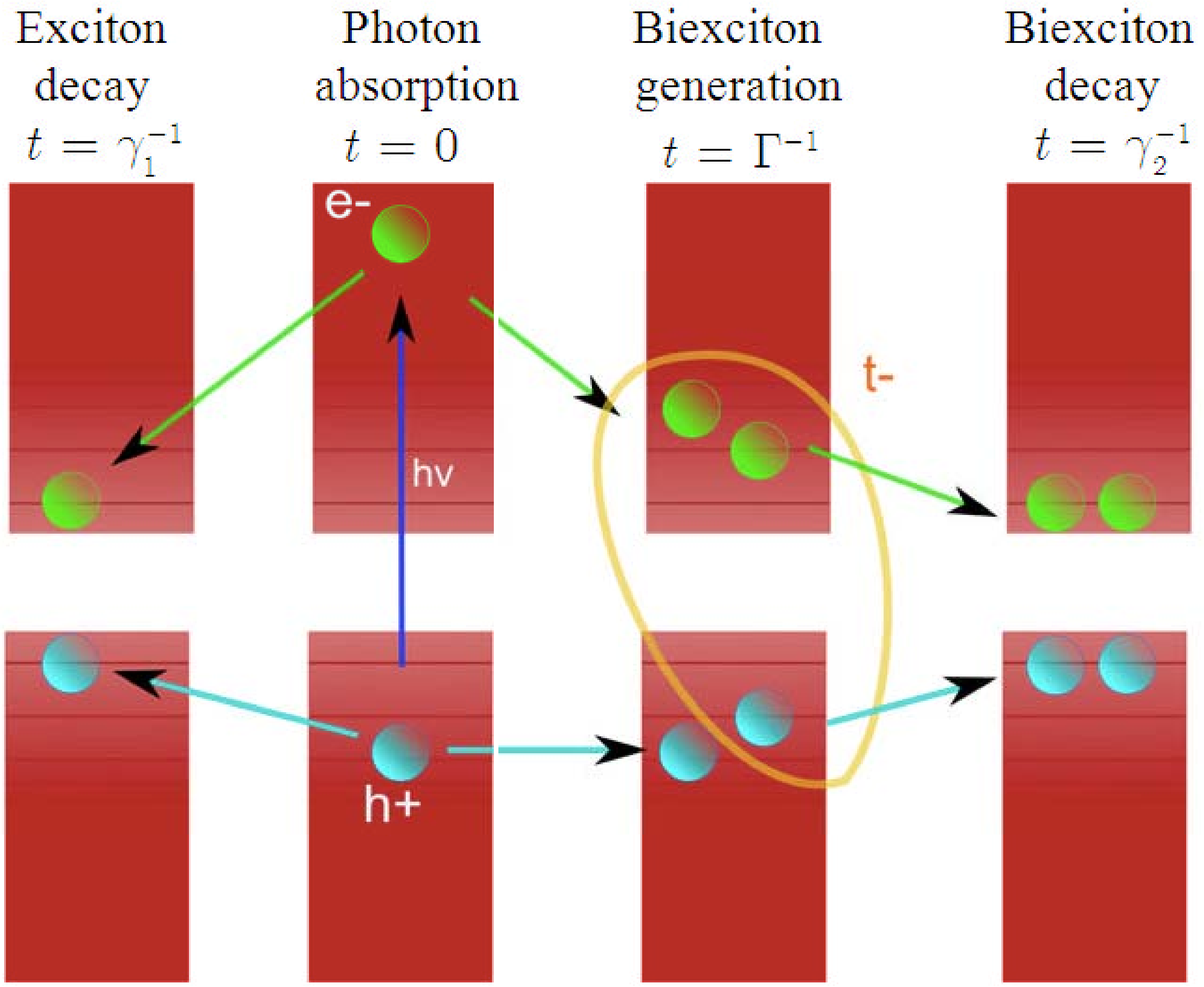
We used the high local electric fields at the junction between the suspended and supported parts of a single carbon nanotube molecule to produce unusually bright infrared emission under unipolar operation. Carriers were accelerated by band-bending at the suspension interface, and they created excitons that radiatively recombined. This excitation mechanism is ~1000 times more efficient than recombination of independently injected electrons and holes, and it results from weak electron-phonon scattering and strong electron-hole binding caused by one-dimensional confinement. The ensuing high excitation density allows us to observe emission from higher excited states not seen by photoexcitation. The excitation mechanism of these states was analyzed.

18 NOVEMBER 2005 VOL 310 SCIENCE



Hot Carrier Impact Exciton generation rate 10^{+15} s^{-1}

1. High MEG: Either increase electron-electron interaction or slow down vibrational relaxation of “hot” Electron



Direct electrical current collection from strong MEG in Carbon Nanotubes

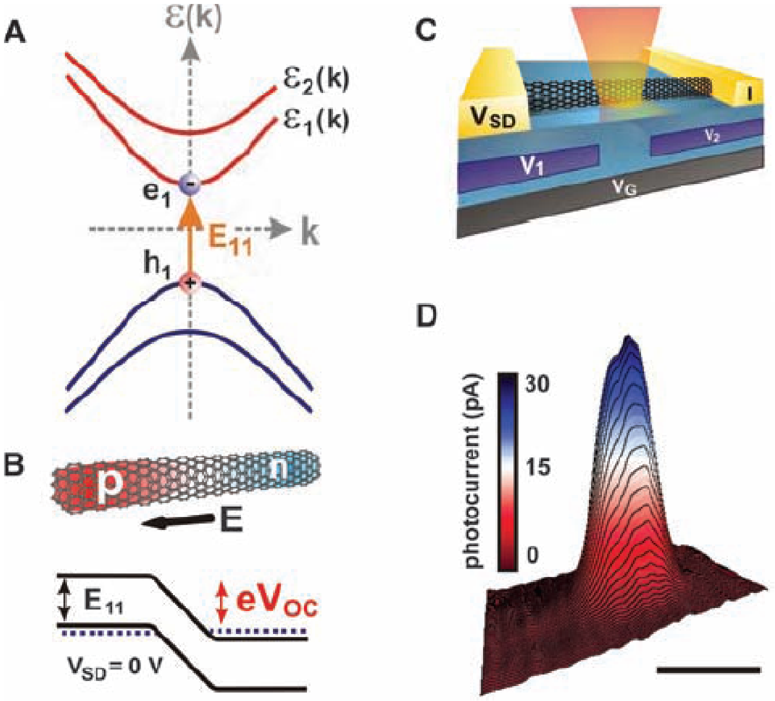
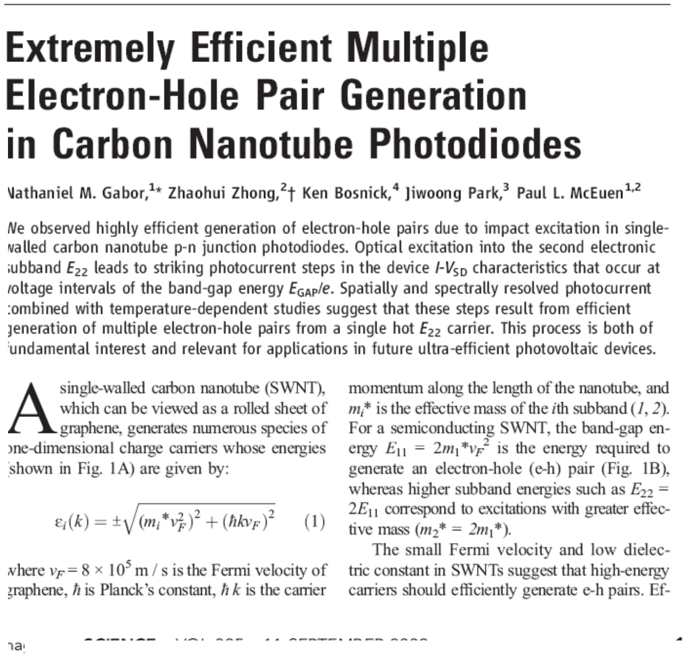


Fig. 1. Band structure, device geometry, and spatial photocurrent of the carbon nanotube p-n junction photodiode. (**A**) Electronic band structure diagram of the carbon nanotube showing electron-hole pair creation into the first subband ε_1 of the nanotube. e_1 labels the electron (blue) and h_1 labels the hole (red) of masses m_1^*. (**B**) (Top) Schematic of the carbon nanotube showing p-type (positive, red) and n-type (negative, blue) regions with built-in electric field E. (Bottom) Length-dependent potential energy diagram of p-n junction at V_{SD} = 0 V. Dotted lines represent the electron Fermi energy in the p- and n- type regions of the device, E_{11} is the band-gap energy, and eV_{OC} is the magnitude of the open-circuit voltage potential. (**C**) Experimental schematic of split-gate device under focused optical illumination. (**D**) Spatially resolved photocurrent map at T = 50 K with continuous wave laser excitation λ = 532 nm and optical power density 25 W/cm^2 for a device of diameter d = 1.8 nm ($V_1 = -V_2 = -9.0$ V; $V_G = V_{SD} = 0.0$ V). Scale bar, 1 μm.



Extremely Efficient Multiple Electron-Hole Pair Generation in Carbon Nanotube Photodiodes

Nathaniel M. Gabor,[1]* Zhaohui Zhong,[2]† Ken Bosnick,[4] Jiwoong Park,[3] Paul L. McEuen[1,2]

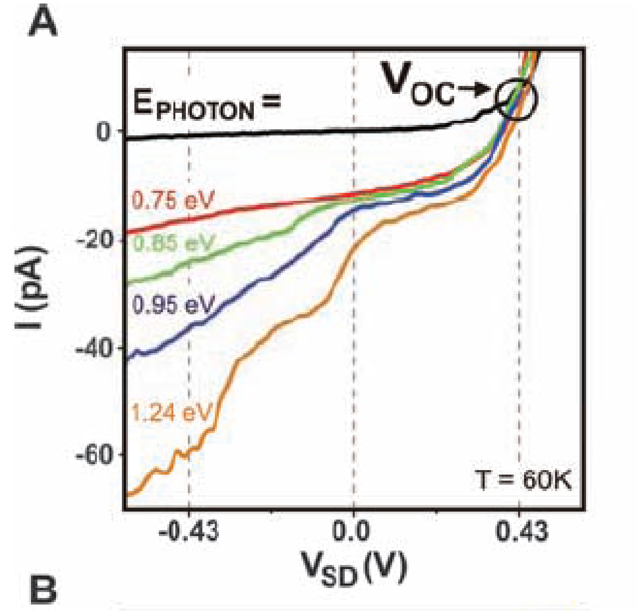
We observed highly efficient generation of electron-hole pairs due to impact excitation in single-walled carbon nanotube p-n junction photodiodes. Optical excitation into the second electronic subband E_{22} leads to striking photocurrent steps in the device I-V_{SD} characteristics that occur at voltage intervals of the band-gap energy E_{GAP}/e. Spatially and spectrally resolved photocurrent combined with temperature-dependent studies suggest that these steps result from efficient generation of multiple electron-hole pairs from a single hot E_{22} carrier. This process is both of fundamental interest and relevant for applications in future ultra-efficient photovoltaic devices.

A single-walled carbon nanotube (SWNT), which can be viewed as a rolled sheet of graphene, generates numerous species of one-dimensional charge carriers whose energies (shown in Fig. 1A) are given by:

$$\varepsilon_i(k) = \pm\sqrt{(m_i^* v_F^2)^2 + (\hbar k v_F)^2} \qquad (1)$$

where $v_F = 8 \times 10^5$ m / s is the Fermi velocity of graphene, $\hbar$ is Planck's constant, $\hbar k$ is the carrier momentum along the length of the nanotube, and m_i^* is the effective mass of the ith subband (*1*, *2*). For a semiconducting SWNT, the band-gap energy $E_{11} = 2m_1^* v_F^2$ is the energy required to generate an electron-hole (e-h) pair (Fig. 1B), whereas higher subband energies such as $E_{22} = 2E_{11}$ correspond to excitations with greater effective mass ($m_2^* = 2m_1^*$).

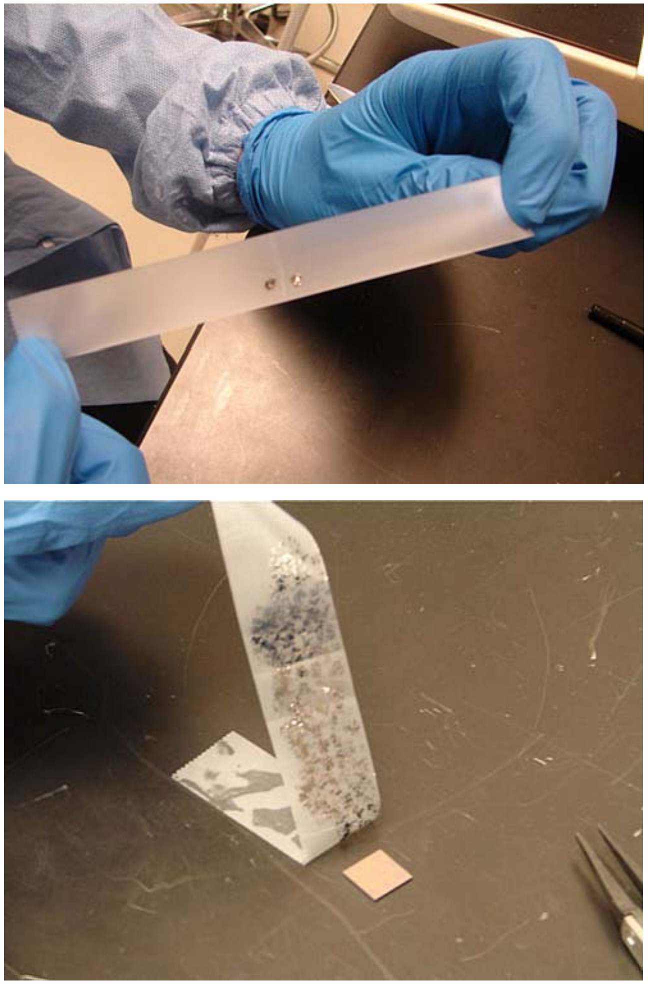
The small Fermi velocity and low dielectric constant in SWNTs suggest that high-energy carriers should efficiently generate e-h pairs. Ef-



Nobel Prize in Physics 2010
Andre Geim and Konstantin Novoselov

For Graphene
Five years from discovery to Nobel Prize!!

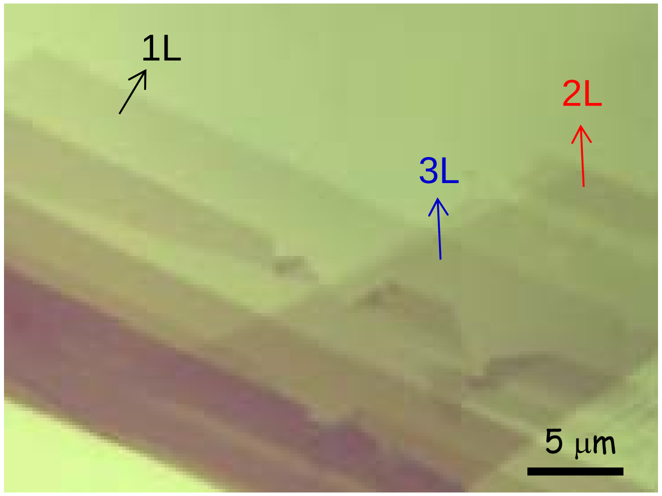
A simple Nobel Prize experiment



-Scientific American
@ Columbia University

Micro-mechanical exfoliation

using “Scotch tape”



Kish graphite on 300 nm SiO_2/Si

Novoselov, Geim et al. PNAS 102, 10452 (2005)

Large Scale CVD Grown Graphene

Graphene/ Ni

Jing Kong Group (MIT)

A. Reina et al., Nano Letters (2009)

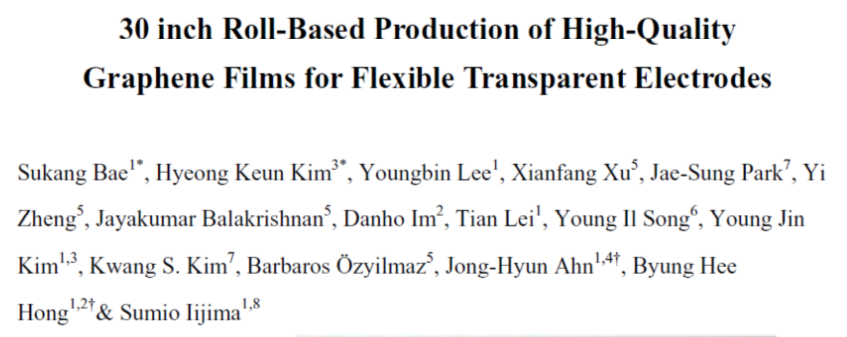
Byung Hee Hong Group (SKK

K. Kim et al., Nature (2009)

Graphene/ Cu

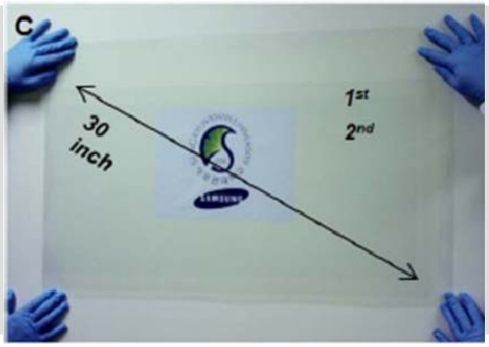
Rod Ruoff Group (Austin)

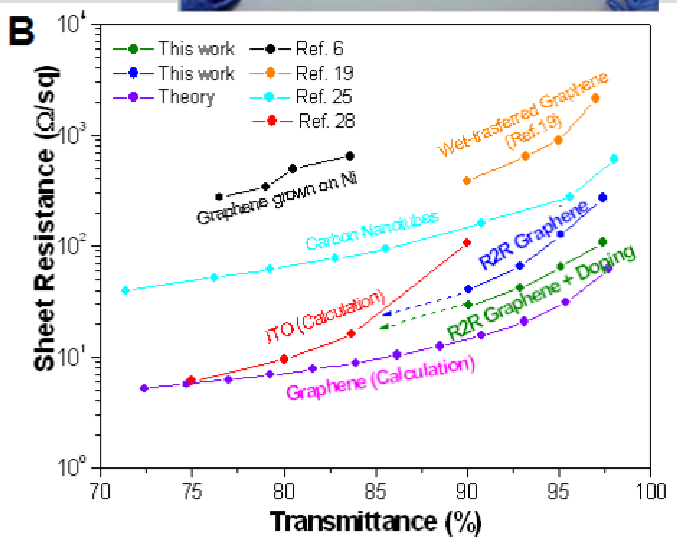
X. Li et al., Science (2009)



30 inch Roll-Based Production of High-Quality Graphene Films for Flexible Transparent Electrodes

Sukang Bae[1*], Hyeong Keun Kim[3*], Youngbin Lee[1], Xianfang Xu[5], Jae-Sung Park[7], Yi Zheng[5], Jayakumar Balakrishnan[5], Danho Im[2], Tian Lei[1], Young Il Song[6], Young Jin Kim[1,3], Kwang S. Kim[7], Barbaros Özyilmaz[5], Jong-Hyun Ahn[1,4†], Byung Hee Hong[1,2†] & Sumio Iijima[1,8]





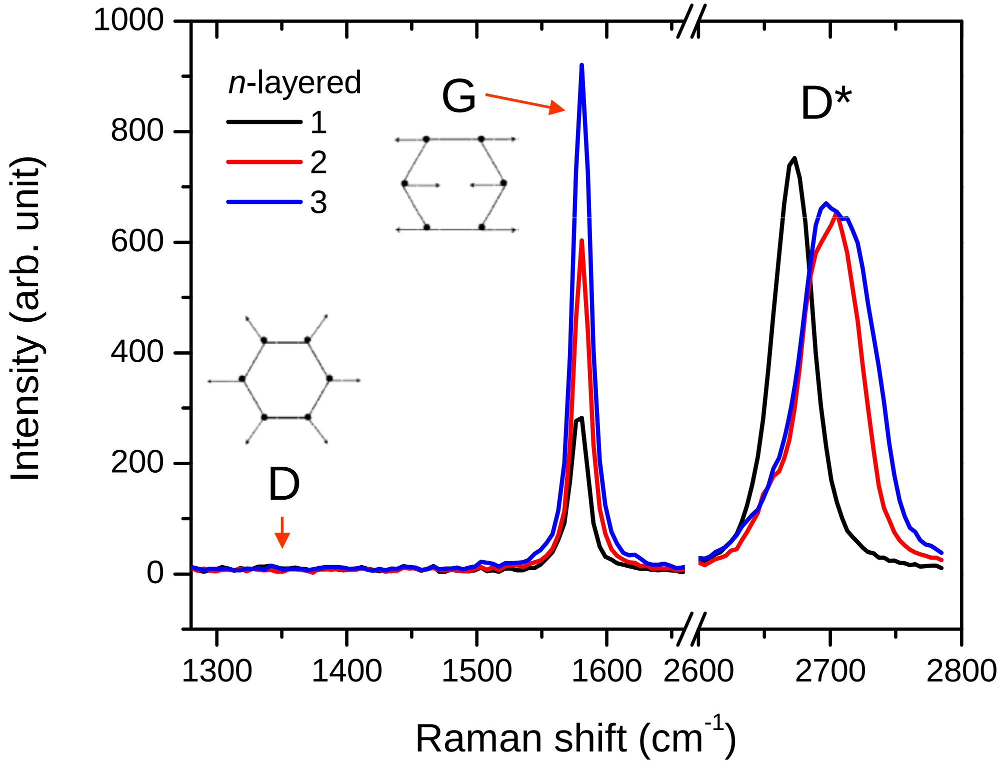
Molecules adsorbed on Graphene:

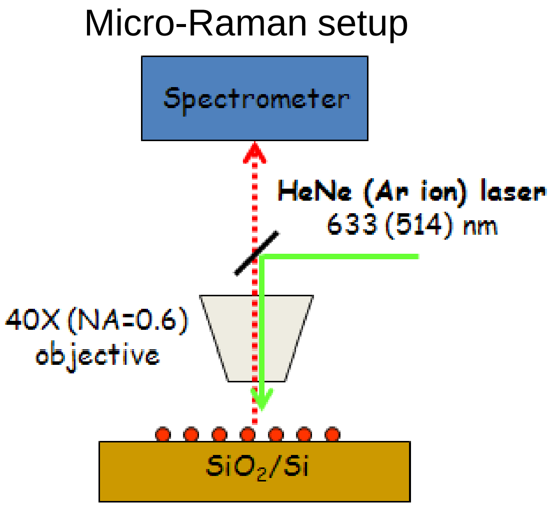
Strong charge transfer electrical doping

Strongly doped graphene is very different than neutral graphene:

Increased in plane DC conductivity, and decreased optical absorption in IR and Visible

Strong G band Resonance Raman scattering, coupled to interband electronic transitions





- A. Ferrari *et al. PRL* (2006)
- J. Yan *et al. PRL* (2007)
…

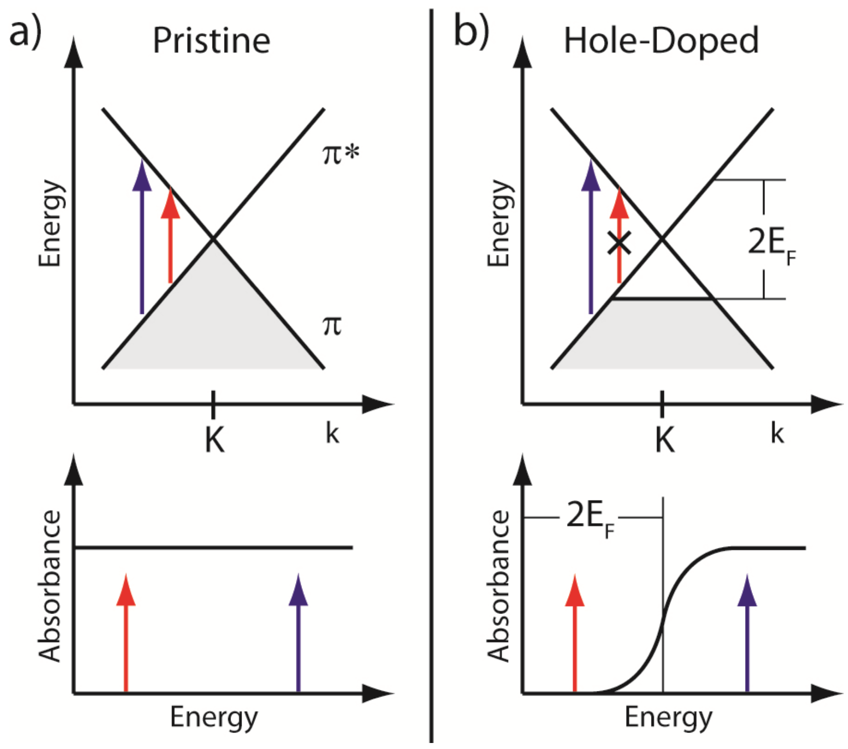
- G mode: C-C stretching (~1580 cm^{-1})

Resonant and off-resonant intensity enhancement:

D. Basko, N. J. Phys. 11, 095011 (2009)

- D mode: ring-breathing (~1350 cm^{-1}) activated by structural defects – sp2 carbon to sp3 carbon
- D* mode: overtone of D mode (~2700 cm^{-1}) indicates thickness

Doping bleaches the electronic spectrum, and shifts the Raman G band



Feng Wang

Uniqueness of graphene:

- All electrons are confined in a single atomic layer:

<u>large electron density change for given gate voltage.</u>

- Small density of states close to Dirac point:

<u>large fermi energy shift for given electron density change.</u>

E_F shift of hundreds of meV:

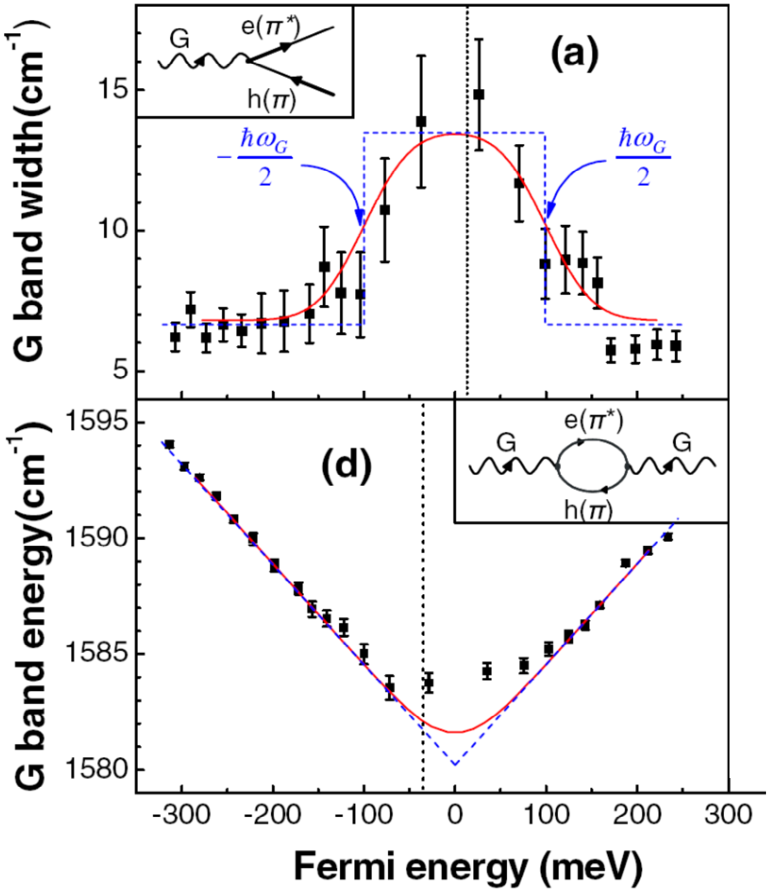
Bleach Optical transitions into near infrared and visible

Shift position of G Raman line

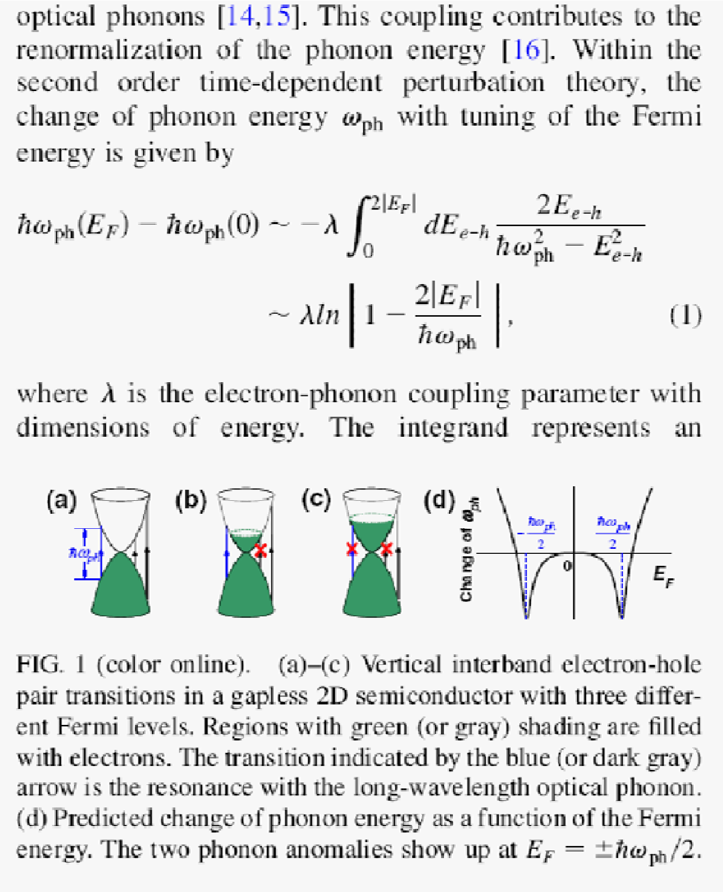
Failure of Born-Oppenheimer Separation of Vibrational and Electronic Degrees of Freedom

- Phonon energy renormalization: ω_G ↑ when $|E_F|$ ↑

- Narrowing of the the G band width



Charge transfer shifts much larger


optical phonons [14,15]. This coupling contributes to the renormalization of the phonon energy [16]. Within the second order time-dependent perturbation theory, the change of phonon energy ω_{ph} with tuning of the Fermi energy is given by

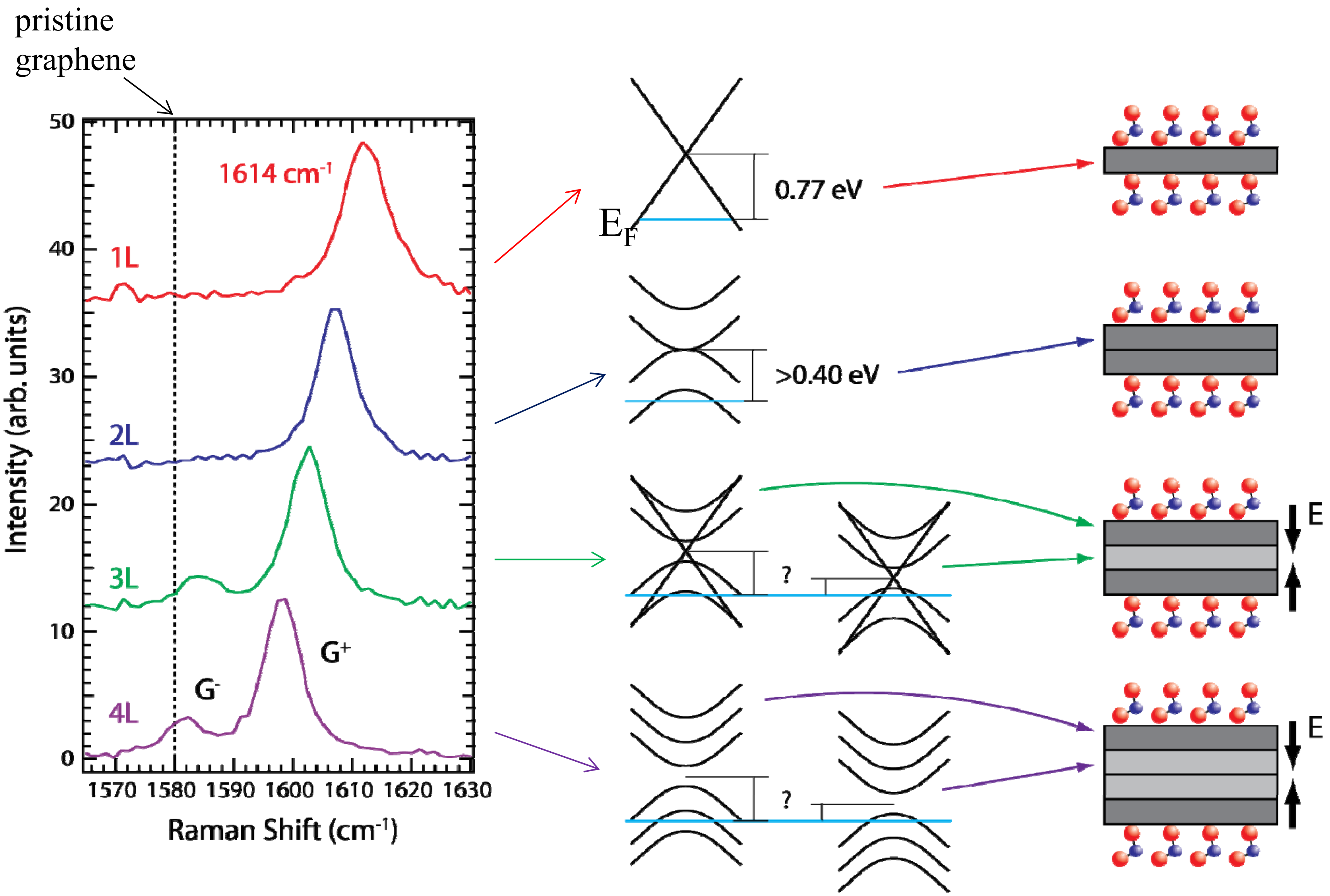
$$\hbar\omega_{\text{ph}}(E_F) - \hbar\omega_{\text{ph}}(0) \sim -\lambda \int_0^{2|E_F|} dE_{e\text{-}h} \frac{2E_{e\text{-}h}}{\hbar\omega_{\text{ph}}^2 - E_{e\text{-}h}^2}$$
$$\sim \lambda ln \left| 1 - \frac{2|E_F|}{\hbar\omega_{\text{ph}}} \right|, \qquad (1)$$

where λ is the electron-phonon coupling parameter with dimensions of energy. The integrand represents an

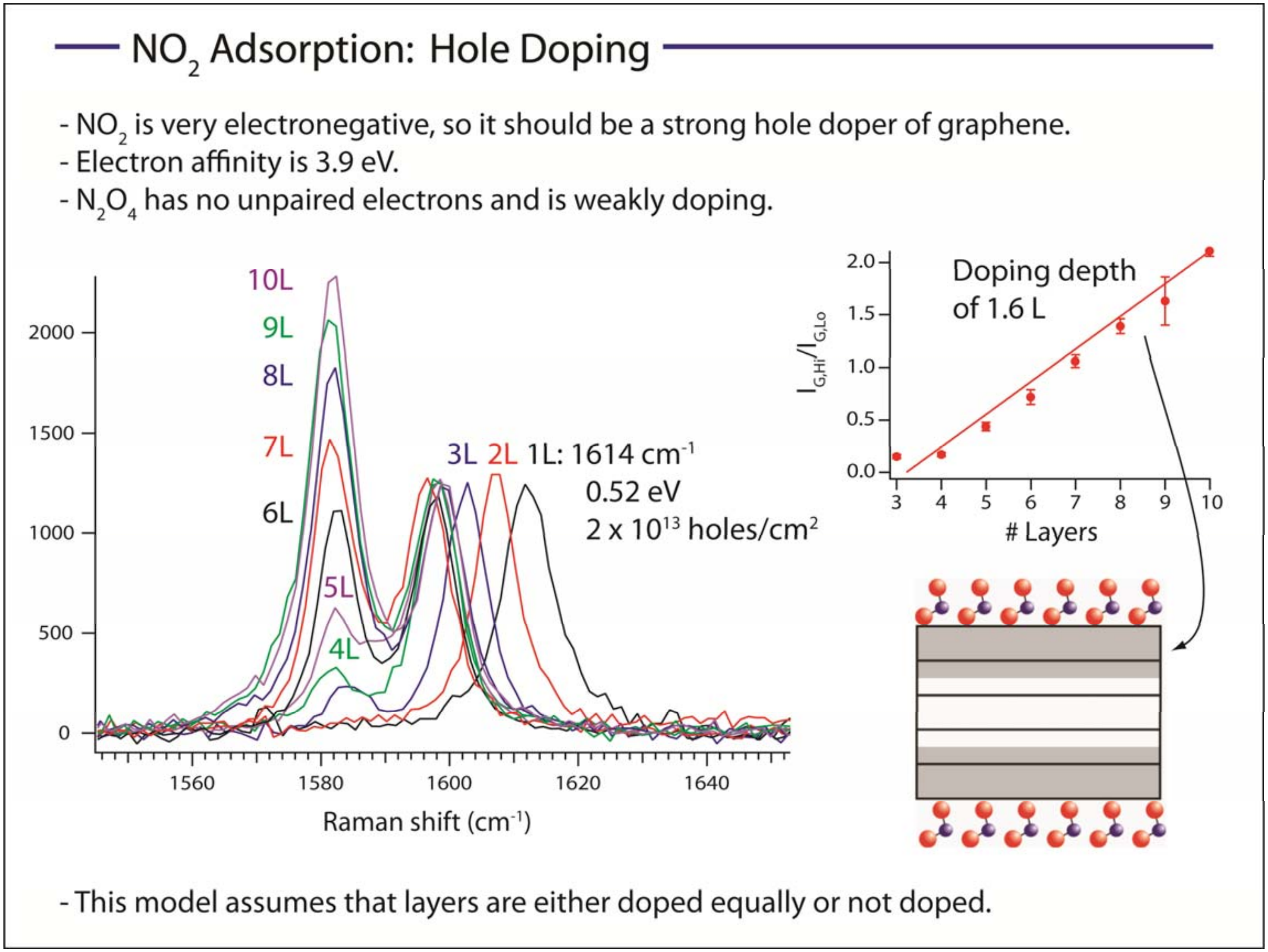
FIG. 1 (color online). (a)–(c) Vertical interband electron-hole pair transitions in a gapless 2D semiconductor with three different Fermi levels. Regions with green (or gray) shading are filled with electrons. The transition indicated by the blue (or dark gray) arrow is the resonance with the long-wavelength optical phonon. (d) Predicted change of phonon energy as a function of the Fermi energy. The two phonon anomalies show up at $E_F = \pm\hbar\omega_{\text{ph}}/2$.

J. Yan et al. PRL **98,** 166802 (2007)
Yan et al, PRL **102**, 136804(2008)
Pinczuk group

NO_2 Adsorption: Surface Hole Doping



Crowther et al, ACS Nano **6**, 1865 (2012)



NO_2 Adsorption: Hole Doping

- NO_2 is very electronegative, so it should be a strong hole doper of graphene.
- Electron affinity is 3.9 eV.
- N_2O_4 has no unpaired electrons and is weakly doping.

- This model assumes that layers are either doped equally or not doped.

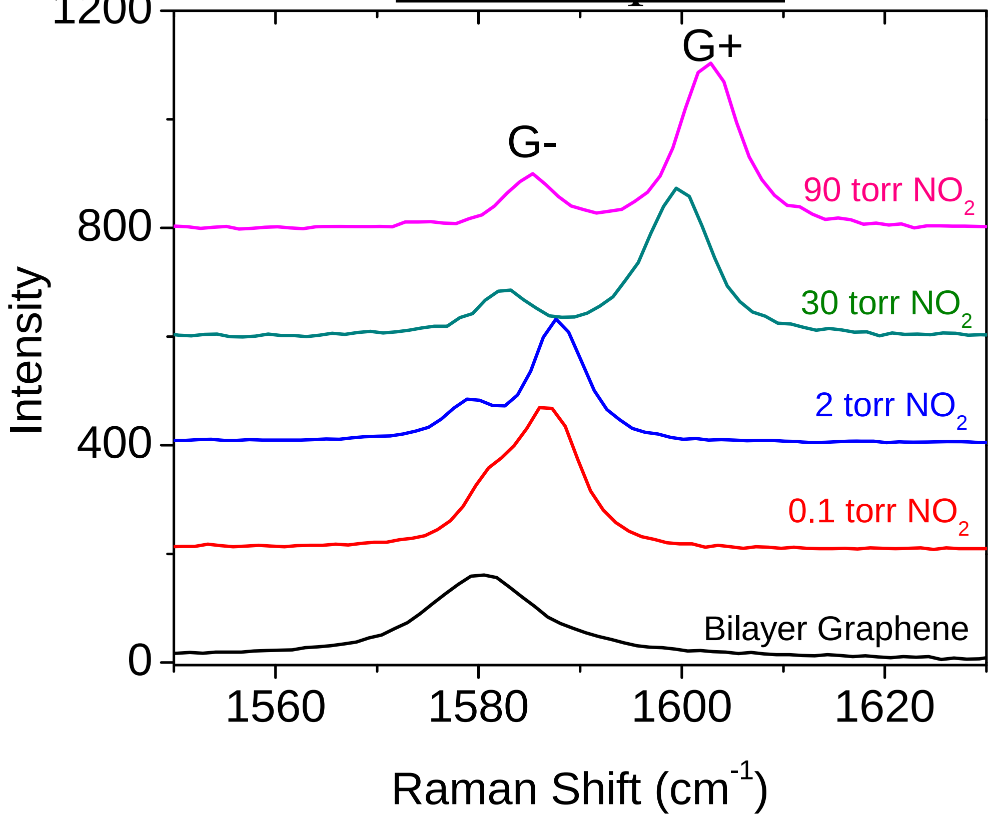
2L shows only one G line: Gas adsorption on both top and bottom layers

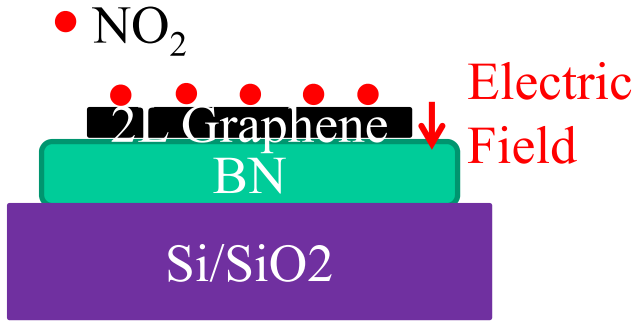
Surface Hole doping extends inside only 1-2 layers

One sided doping of Bilayer Graphene on h-BN

- The Strong graphene-BN interaction blocks diffusion of NO_2 between graphene and BN, introducing one-side doping to bilayer (2L) graphene.

Raman Spectra




● NO_2

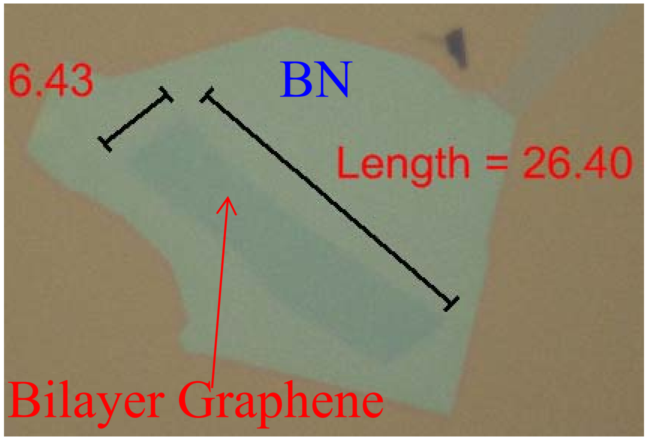
Electric Field

2L Graphene

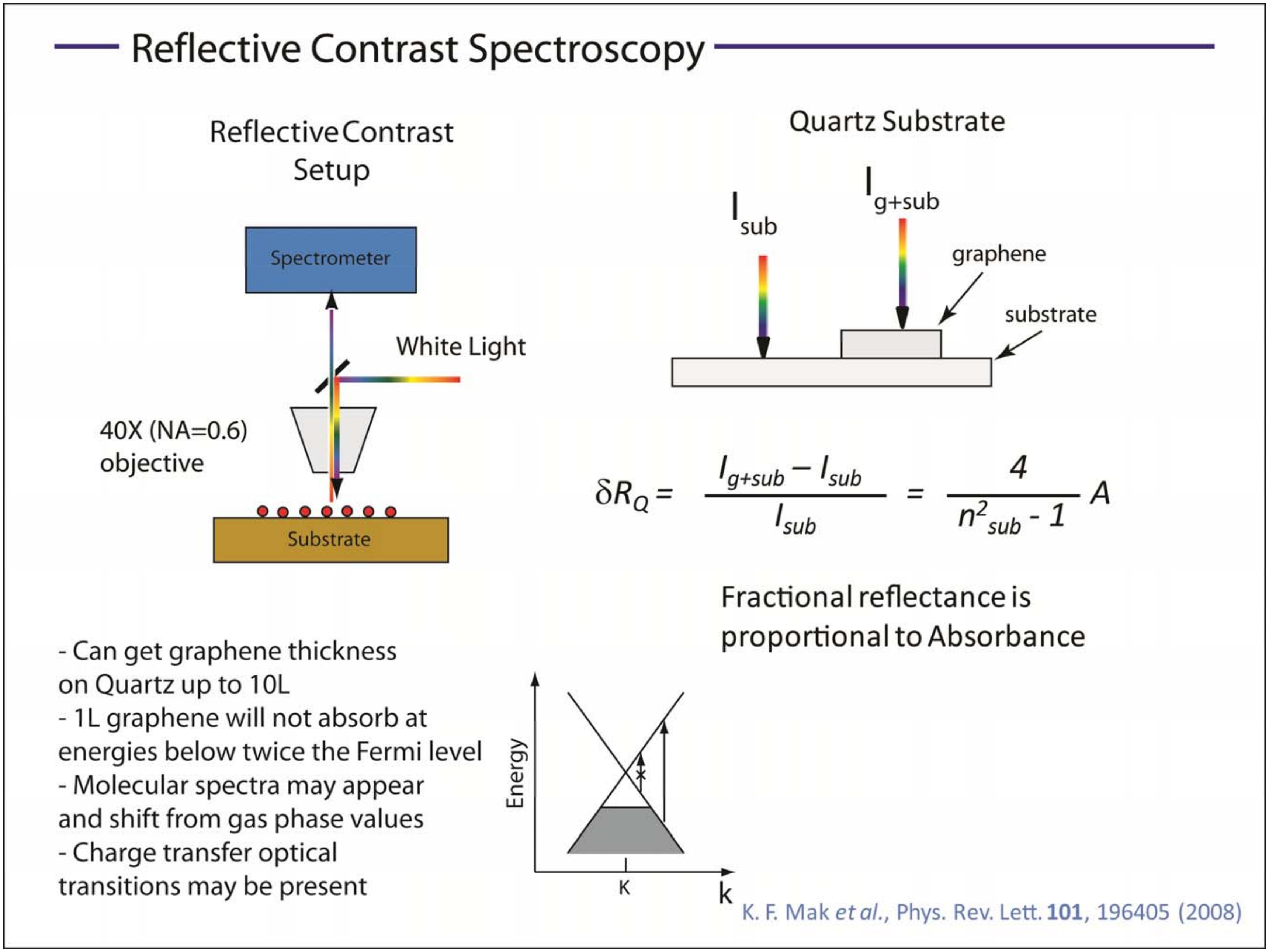
BN

Si/SiO2

Optical Image



Direct observation of Optical Bleach Due to Hole Doping



Reflective Contrast Spectroscopy

Reflective Contrast Setup

40X (NA=0.6) objective

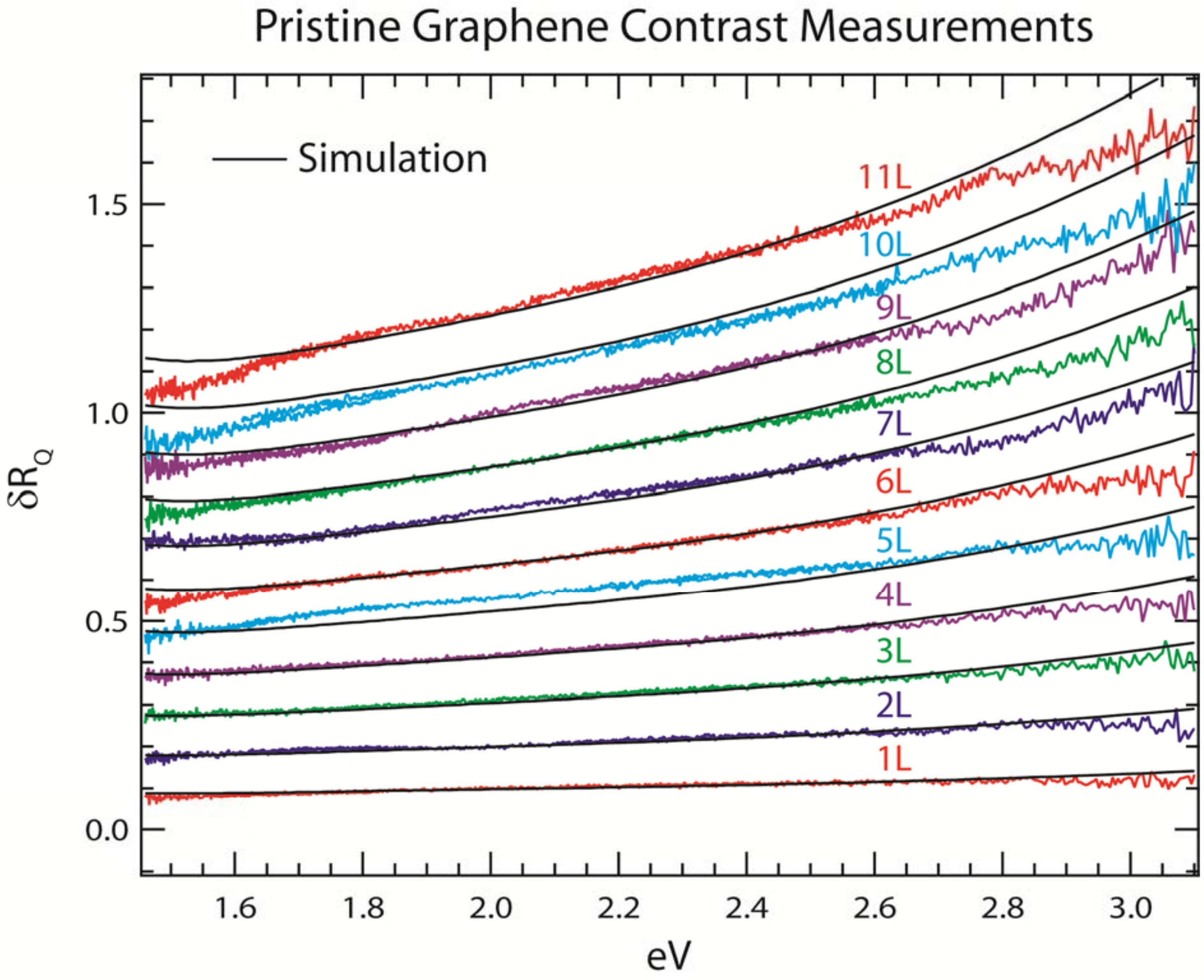
Quartz Substrate

$$\delta R_Q = \frac{I_{g+sub} - I_{sub}}{I_{sub}} = \frac{4}{n^2_{sub} - 1} A$$

Fractional reflectance is proportional to Absorbance

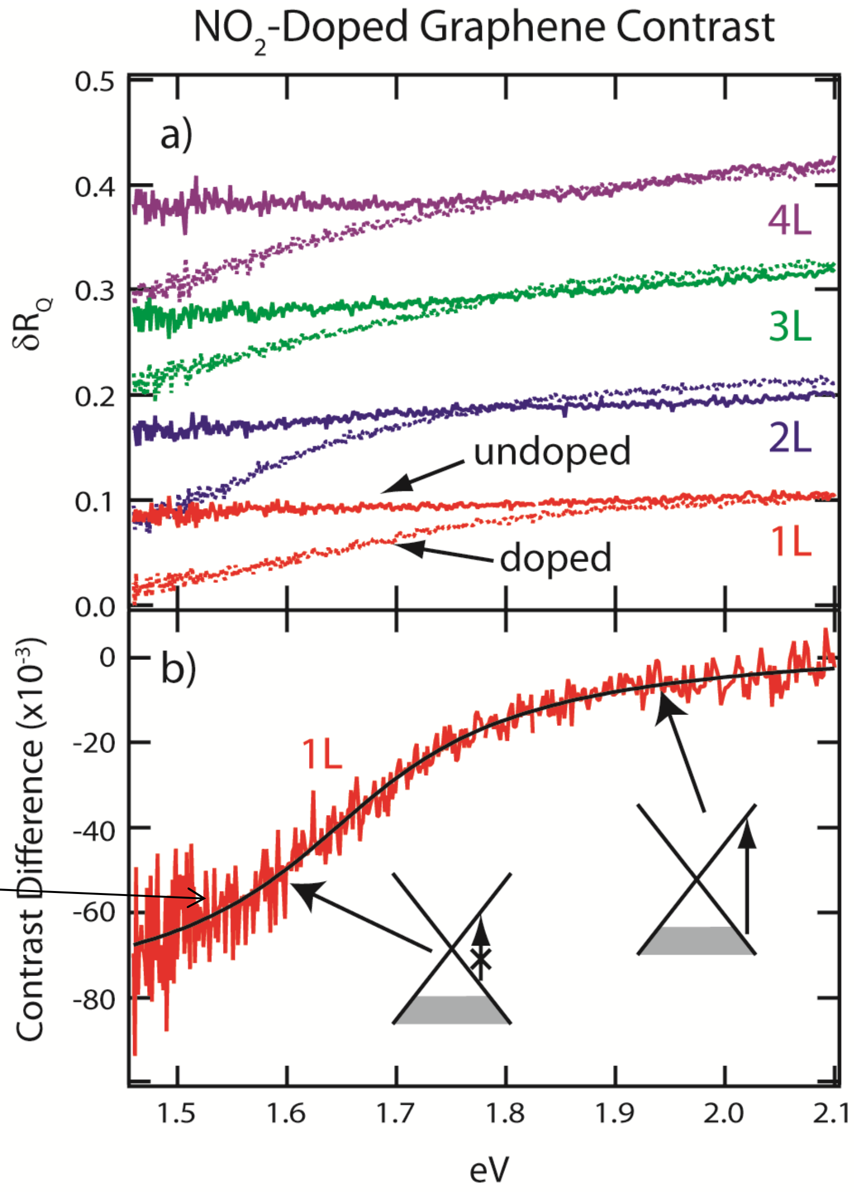
- Can get graphene thickness on Quartz up to 10L
- 1L graphene will not absorb at energies below twice the Fermi level
- Molecular spectra may appear and shift from gas phase values
- Charge transfer optical transitions may be present

K. F. Mak *et al.*, Phys. Rev. Lett. **101**, 196405 (2008)


Pristine Graphene Contrast Measurements
Simulation
11L
10L
9L
8L
7L
6L
5L
4L
3L
2L
1L
δR_Q
1.5
1.0
0.5
0.0
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
eV

Bleaching of electronic absorption due to surface hole doping

In 1L graphene, Fermi level shift
Of about 0.75 eV from both the Ram
Shift and the electronic bleach



Bleach due to hole doping

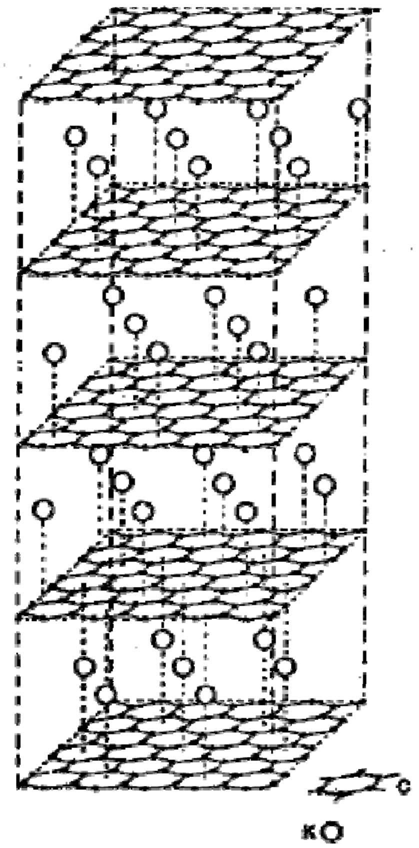
Molecules between the layers: Graphite Intercalation Compounds

$FeCl_3$, Br_2, I_2, NO_2 K, Rb, Li, Ca

Donor: Alkali Metal, Alkaline earth metals, lanthanides.

Acceptor: Lewis acid Intercalants (Halogens, Acidic Oxides, Strong Bronsted acids)

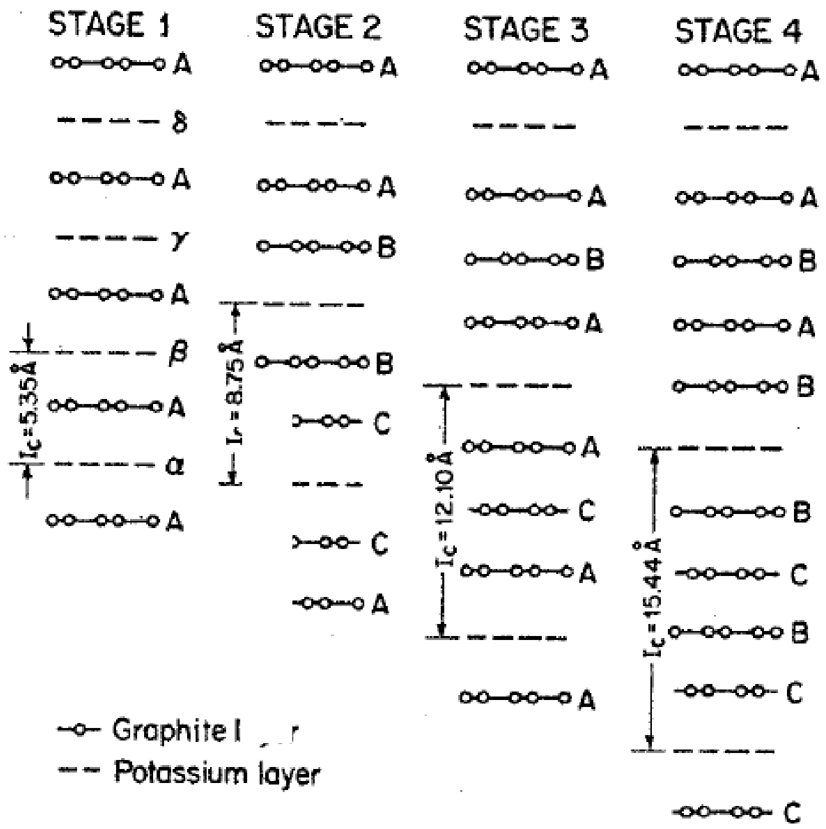
- More than 100 reagents can be intercalated into graphite.



Dresselhaus. Adv. Phys. 51, 1 (2002)

Bromine forms a stage 2 Bulk Intercalation Compound

Bromine



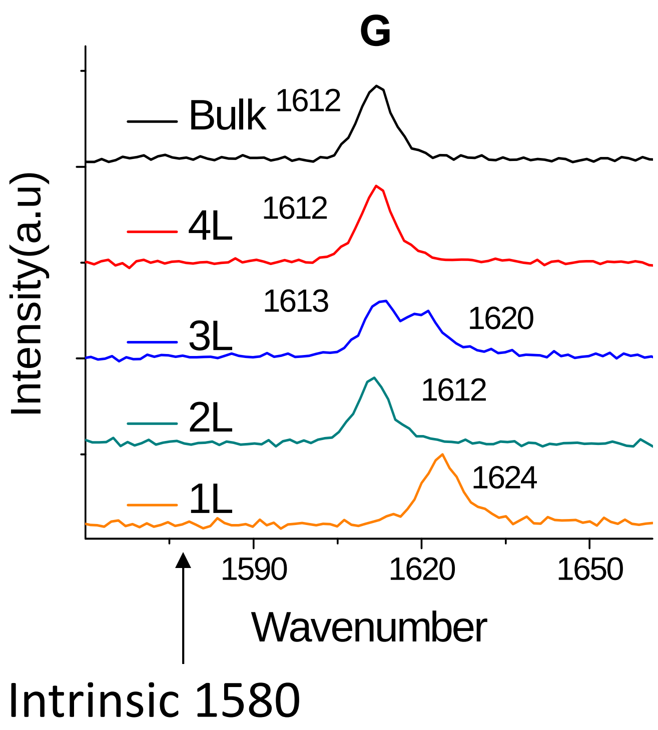
Graphene

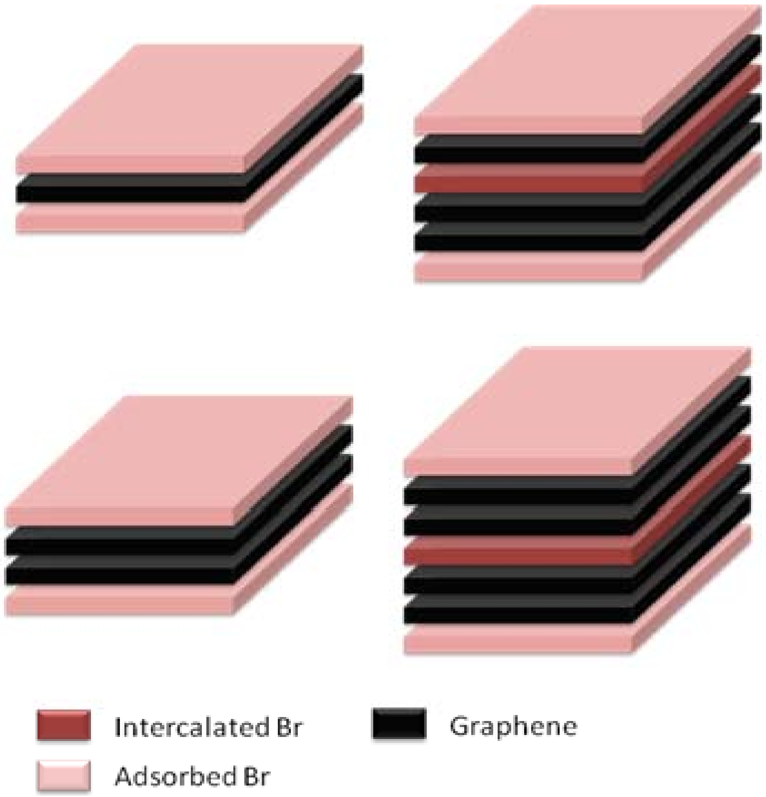
Intercalate Layer

- Stage # : The number of graphene layers per intercalate layer.
- Doping level varies layer to layer

Dresselhaus. Adv. Phys. 51, 1 (2002)

Br_2 Vapor Exposed Graphene: both intercalation and adsorption



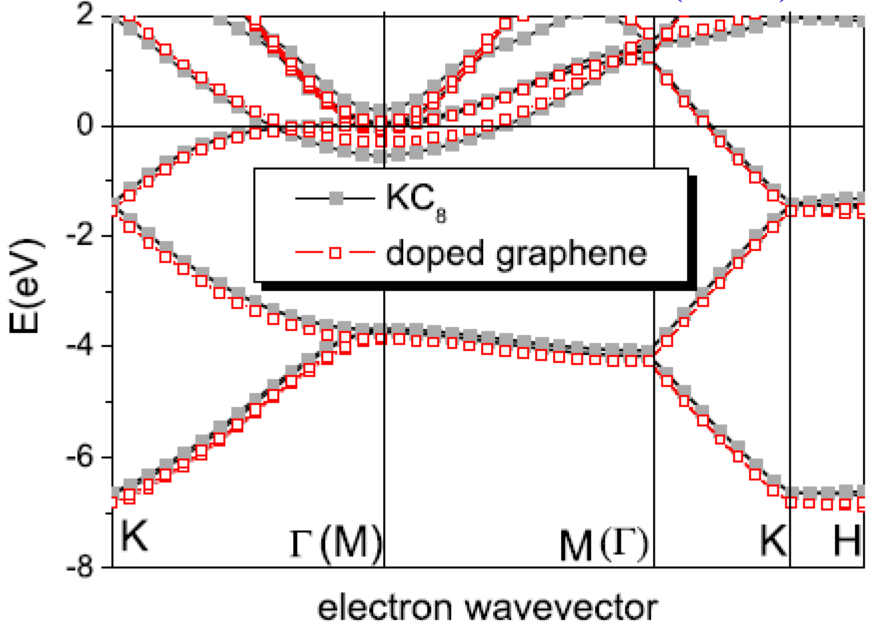


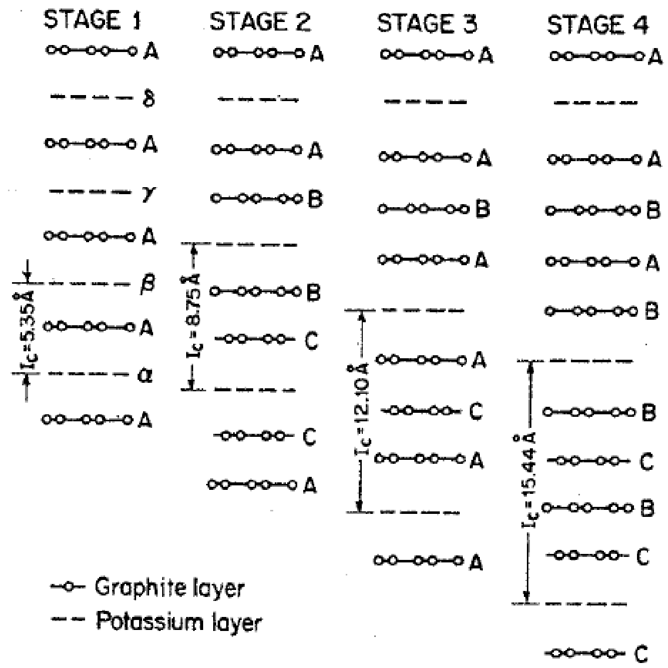
- G peak up-shift as charge density of graphene increases
- Stage 2 Intercalation observed similar to Bulk HOPG.
- Bromine intercalates 3L and higher nL
- 1L G peak shifts the most due to two layers of adsorption, on the top and bottom of graphene.
- 2L, 4L, and Graphite show same charge transfer amount.

N. Jung et al Nano Letters 9, 4133 (2009)

Very high electron doping: stage 1 alkali intercalation

Gruneis PRB 79 205106 (2009)





Fermi level shifts for C_8Cs, C_8K and C_8Rb are respectively 1.0, 1.4 and 1.8eV.
Graphene Layers are decoupled AA stacking. No band gap at K point.

Fermi level at M point, which is folded back on Gamma point by crystalline alkali intercalation layers

Interband optical absorption completely gone

Intraband Drude free electron optical absorption strong

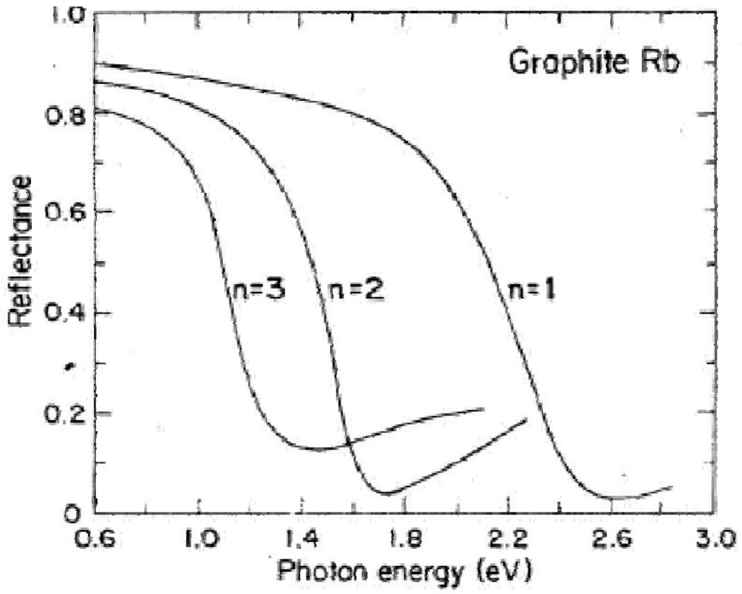
Extreme Electron Doping in bulk Alkali Metal GICs

- Shifts in Fermi level in intercalation compounds can be quite large: Fermi level shifts for Stage 1 C_8Cs, C_8K and C_8Rb are respectively 1.0, 1.4 and 1.8eV. Layers are also decoupled. Expect complete electronic bleaching in the visible spectrum.

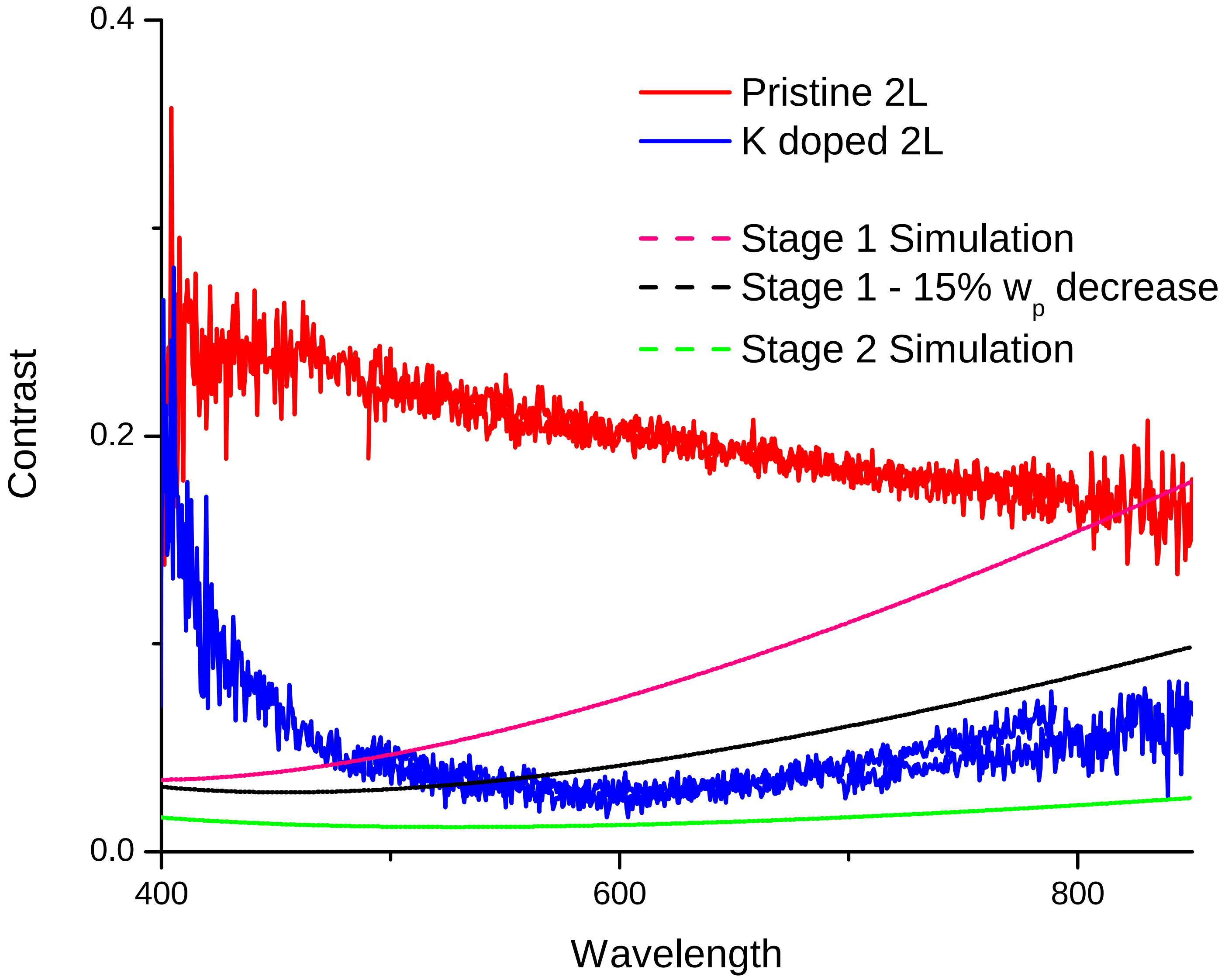
- Free electrons on metal layers and graphene create a 2D Drude electron gas with a plasma edge in the visible spectrum

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^{\ 2}}{\omega(\omega + i/\tau_D)}$$

GIC dielectric constant in the visible and IR is well fit by a Drude free carrier model with , effective plasma frequency and mean carrier lifetime.

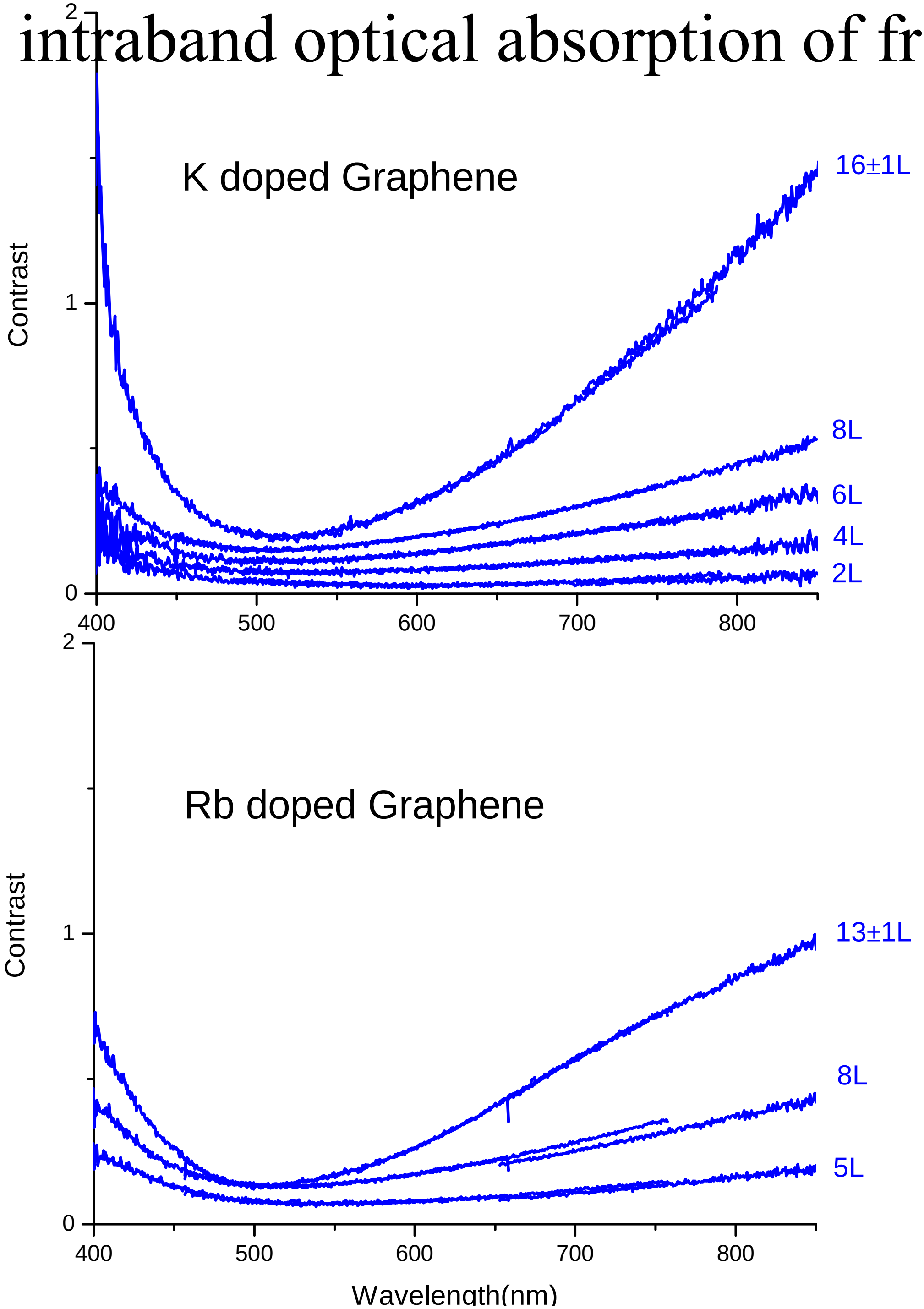


Extreme Bleaching of 2L graphene visible interband optical absorption, at very high electron charge transfer

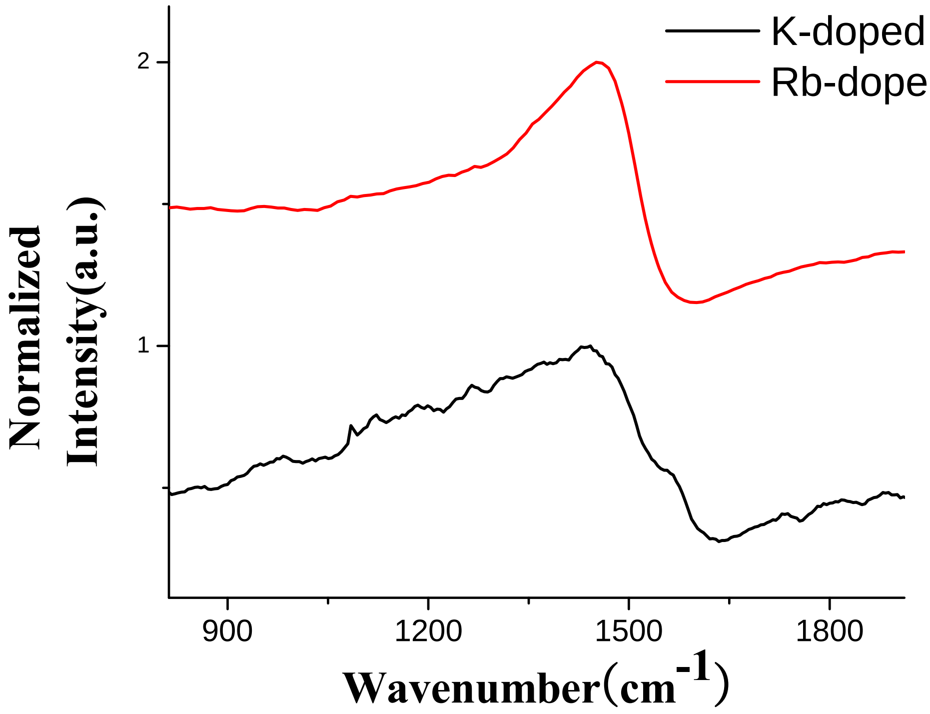


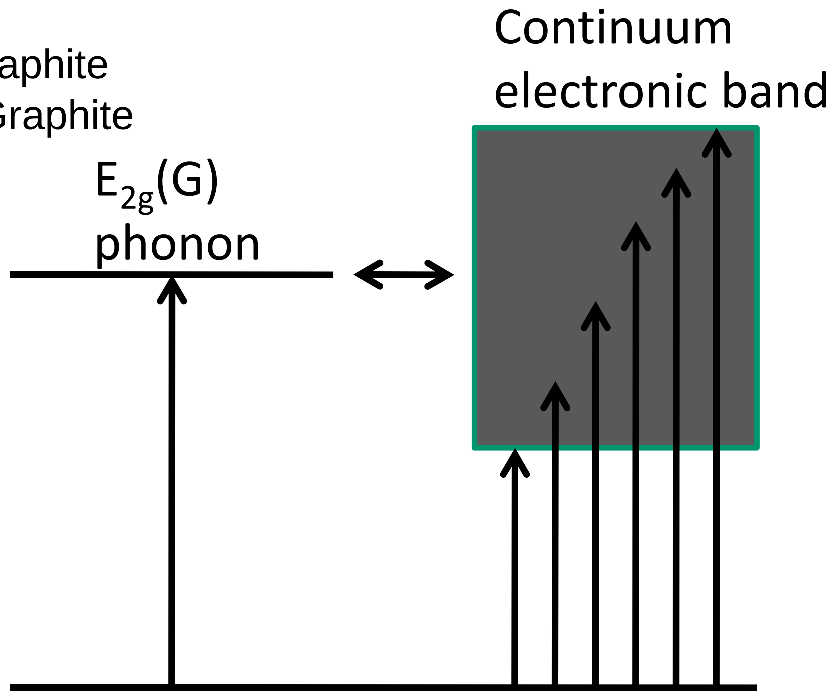
Brus group

Graphene: Drude intraband optical absorption of free electrons



Bulk alkali intercalated graphite:
G band Raman Downshift and Fano Lineshape





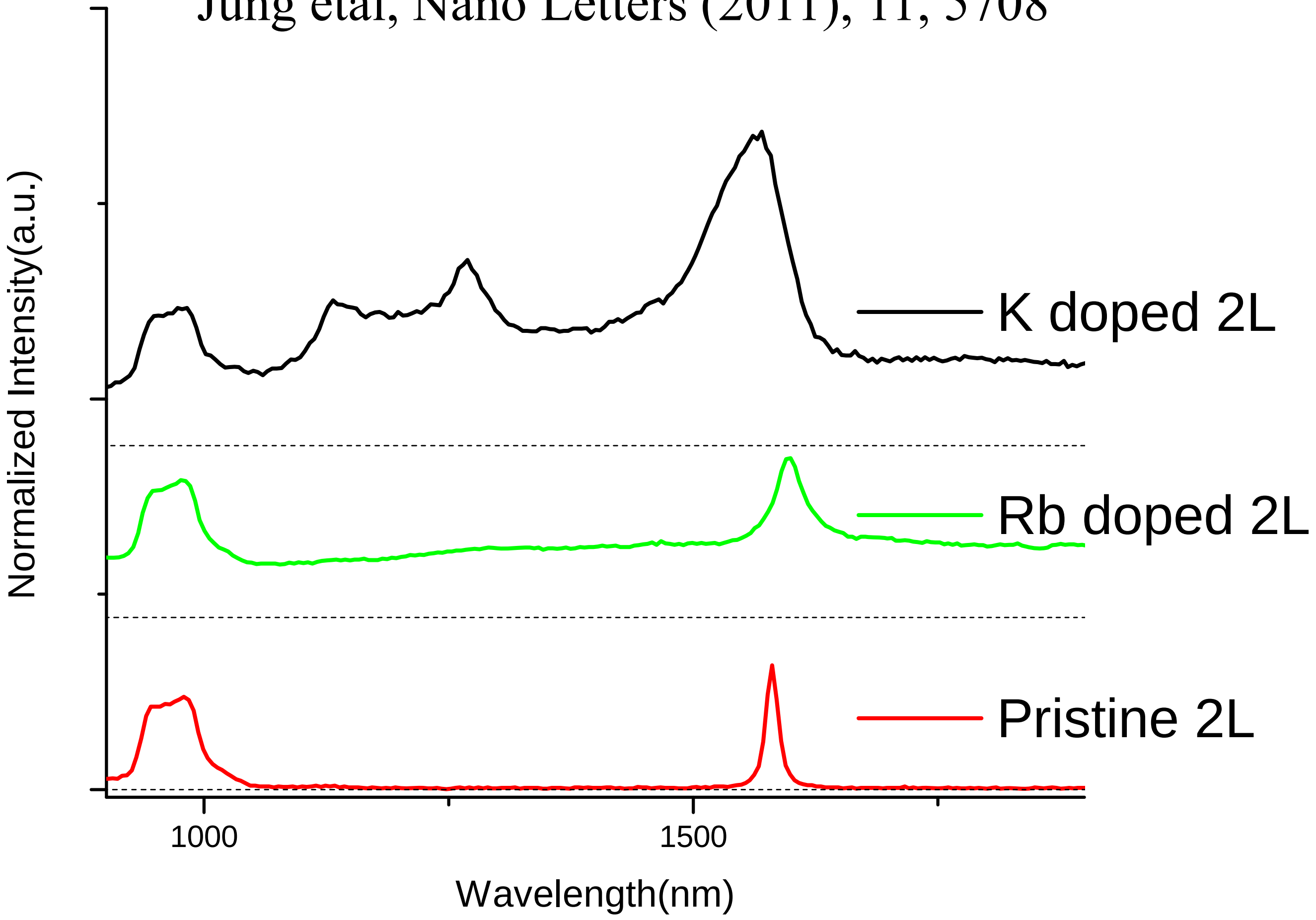
Continuum electronic band

E_{2g}(G) phonon

- The BWF (Breit-Wigner-Fano) Raman shape of G mode in bulk graphite is due to coupling of discrete G phonon to the continuous interlayer electronic band along the k_z axis.

New Raman Spectra for alkali doped Few layer Graphenes

Jung etal, Nano Letters (2011), 11, 5708

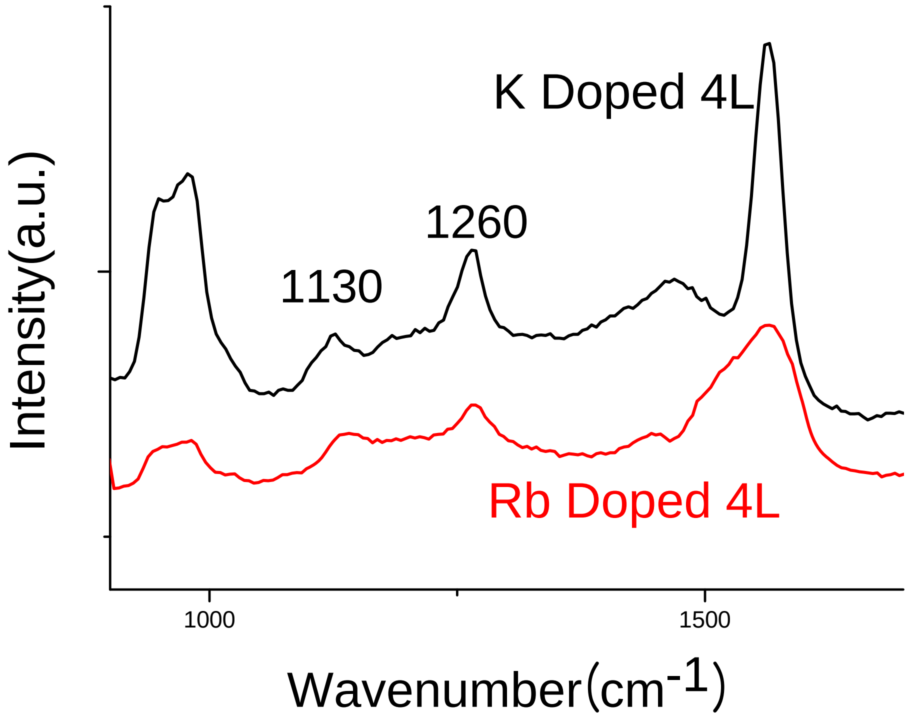


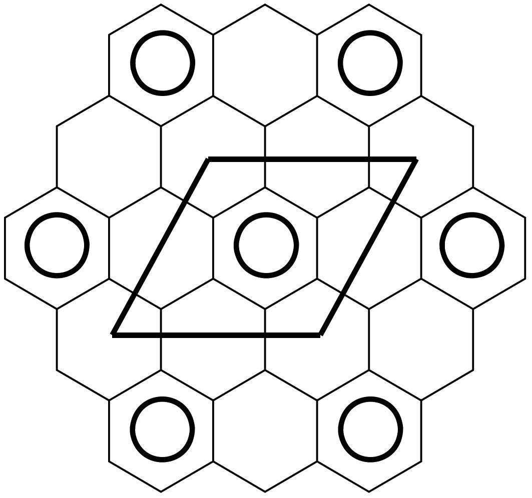
Bulk Fano Raman Lineshape Develops only slowly with increasing thickness

New resonance Raman effect, not from Basko Analyzed interband optical transition

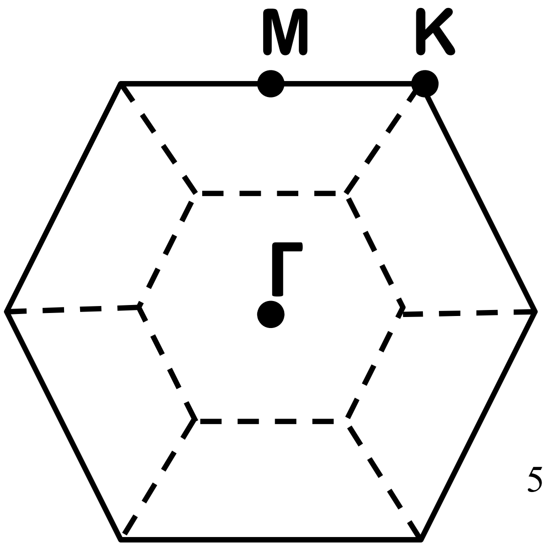
Less electron transfer for few layer graphenes

Intrinsic silent graphene modes activated in Raman by p(2x2) alkali metal zone folding





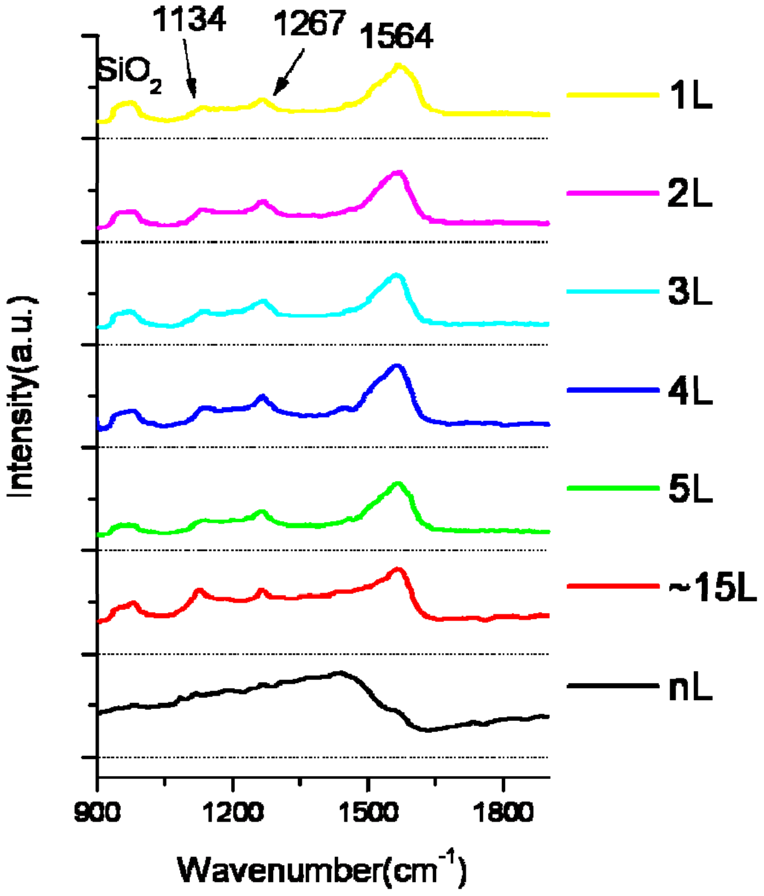
p(2x2) Superlattice



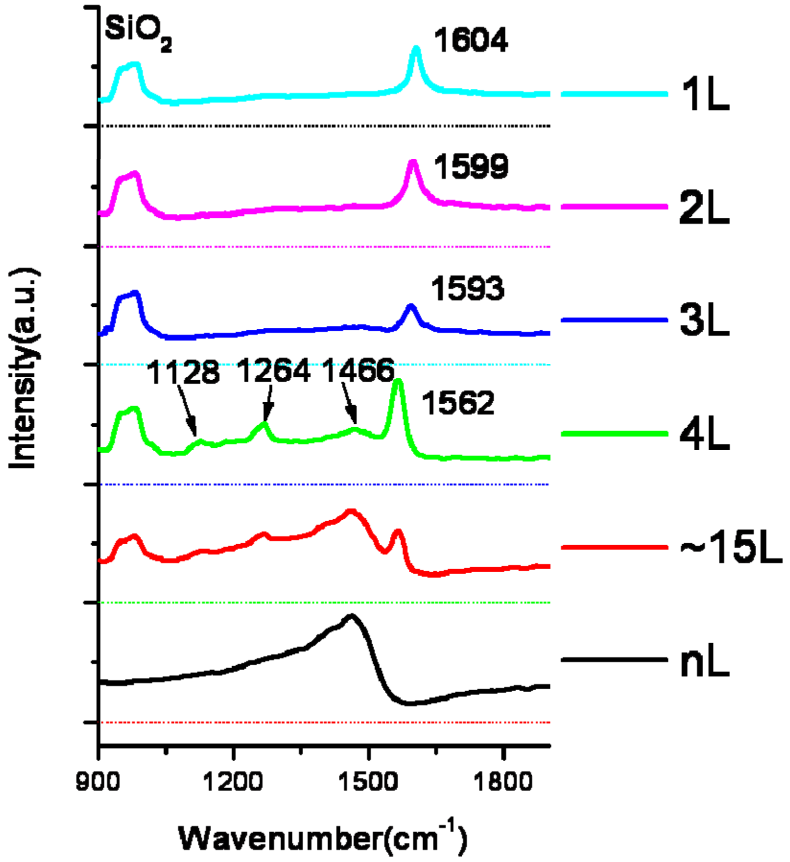
- Potassium and Rubidium intercalated graphene develops the identical Raman peaks at 1130 and 1260 which is due to folded M point Raman.

K and Rb intercalated Few layer Graphene

K-doped



Rb-doped



- While adsorbed potassium fully doped graphene as intercalated layer, adsorbed rubidium does not dope graphene much as potassium does.

Conclusions:

Both CdSe Nanocrystals and SWNT show simple quantum confinement. Electron Correlation is high in graphene and SWNT, but low in CdSe nanocrystals.

High graphene charge doping from molecular absorption, without application of voltage

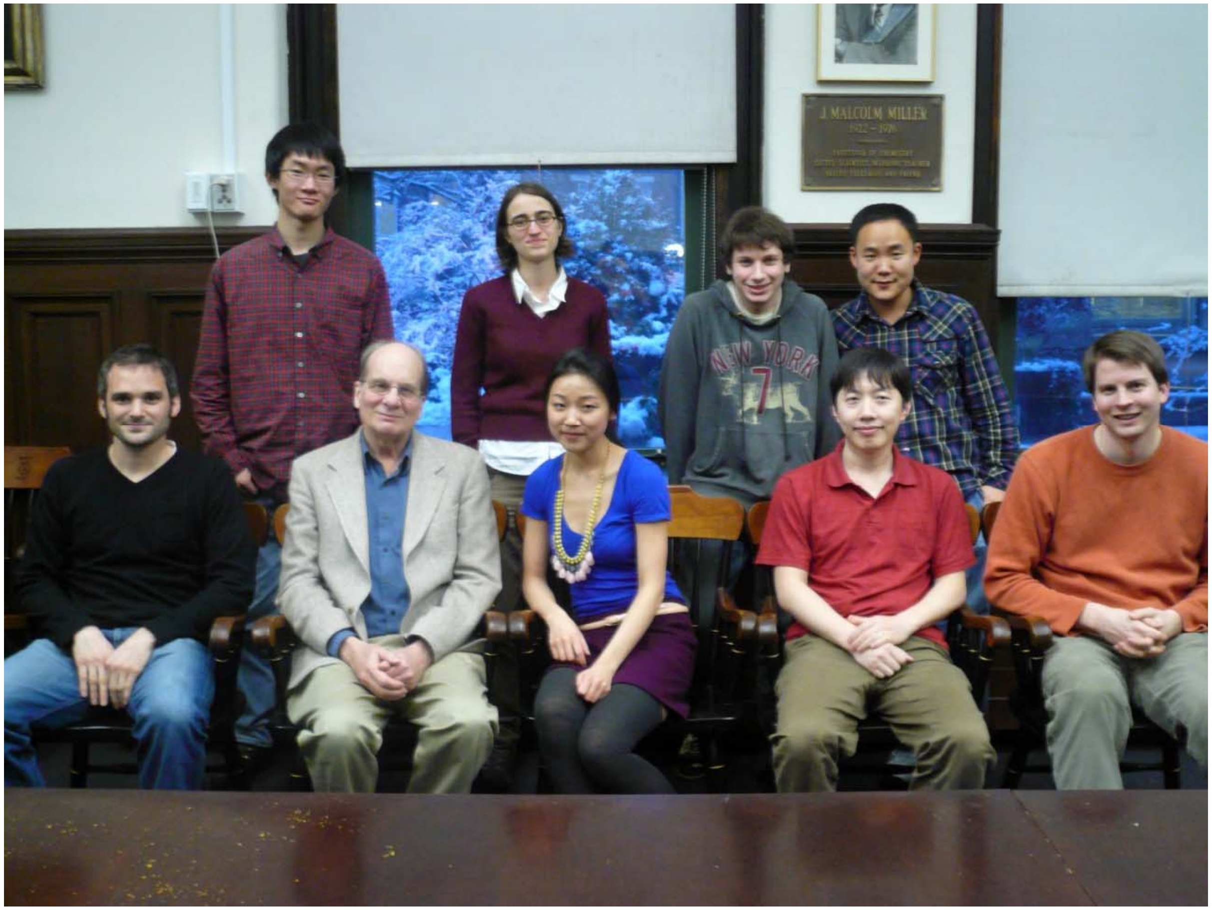
Band bending from surface doping extends one or two graphene layers.

One sided chemical doping can be achieved on BN substrate

With K and Rb stage 1 intercalation, complete bleaching of interband optical absorption occurs in few layer graphenes. Drude optical plasma edge of doped electrons observed in visible.

High charge transfer of stage 1 K intercalated graphite develops only slowly as a function of the number of graphene layers.

Thanks to NSF, DOE, Keck Foundation, AFOSR, collaborators and especially students!



Graphene students and postdocs:

Sunmin Ryu, Stephane Berciaud, Haitao Liu, Andrew Crowther, Naeyoung Jung, Li Liu, Zheyuan Chen, Yinsheng Guo, Elizabeth Thrall